

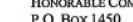
IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of:
TODD ET AL. § Group Art Unit: 1796
Serial No.: 10/664,126 §
Filed: SEPT. 17, 2003 § Examiner: FIGUEROA, JOHN J.
Title: "IMPROVED SUBTERRANEAN § Atty. Docket No: 2003-IP-010228U1
TREATMENT FLUIDS AND METHODS §
OF TREATING SUBTERRANEAN §
FORMATION"

CERTIFICATE OF FILING ELECTRONICALLY VIA EFS
37 C.F.R. § 1.8

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APPELLANTS' BRIEF (37 C.F.R. § 41.37)

This brief is submitted in support of Applicants' Notice of Appeal from the rejections in the Final Office Action dated March 18, 2008 (the "Final Office Action") and the Notice of Panel Decision from Pre-Appeal Brief Review dated August 19, 2008.

The deadline under the shortened statutory period for filing this Appeal Brief is September 19, 2008, pursuant to the Notice of Panel Decision from Pre-Appeal Brief Review. This Appeal Brief is being submitted with a request for a one-month extension of time extending the period for filing to October 19, 2008. Therefore, this Appeal Brief is timely filed.

I. IDENTIFICATION OF THE REAL PARTIES OF INTEREST

The real party in interest is:

Halliburton Energy Services, Inc.
10200 Bellaire Blvd.
Houston, Texas 77072

by virtue of assignments by the inventors as duly recorded in the Assignment Branch of the U.S. Patent and Trademark Office.

II. IDENTIFICATION OF RELATED APPEALS AND INTERFERENCES

There are no related appeals or interferences, to Appellants' knowledge.

III. STATUS OF THE CLAIMS

The application as originally filed contained 68 claims. Claims 1-14, 19, 32-46, and 69-81 were cancelled in a previous response. Claims 24-27, 31, 51-54, and 68 have been withdrawn in response to the Examiner's restriction requirement. Claims 15-18, 20-23, 28-30, 47-50, and 55-67 are pending.

The Examiner has finally rejected claims 15-18, 20-23, 29, 30, 47-50, 56-64, 66, and 67 under 35 U.S.C. § 102(b) as being anticipated by U.S. Patent No. 6,387,986 to Moradi-Araghi *et al.* ("Moradi-Araghi").¹ Appellants disagree with these rejections.

The Examiner also has finally rejected claims 15, 23, 28, 47, 50, 55, and 65 under 35 under 35 U.S.C. § 103(a) as being unpatentable over *Moradi-Araghi* in view of U.S. Patent No. 5,728,652 to Dobson *et al.* ("Dobson"), U.S. Patent No. 5,191,931 to Himes *et al.* ("Himes"), or U.S. Patent No. 4,531,594 to Cowan ("Cowan"). Appellants disagree with these rejections.

Appellants herein appeal the final rejections of claims 15-18, 20-23, 28, 29, 30, 47-50, 55-67 as improperly rejected. A listing of all appealed claims is provided in Appendix A in this Brief.

IV. STATUS OF ANY AMENDMENT FILED SUBSEQUENT TO FINAL REJECTION

No amendment has been filed subsequent to final rejection.

V. SUMMARY OF THE CLAIMED SUBJECT MATTER

Appellants' invention relates to bridging agents for use in subterranean formations, to well drill-in and servicing fluids comprising such bridging agents, and to methods

¹ A copy of *Moradi-Araghi* is attached as Appendix E to this Brief.

of using such bridging agents and well drill-in and servicing fluids in subterranean drilling operations. (See Specification at page 4, ll. 1-4).²

Certain embodiments of Appellants' invention provide methods of drilling an open hole in a subterranean formation. These methods comprise the steps of: circulating through the drill pipe and drill bit a well drill-in and servicing fluid comprising a viscosified fluid, a fluid loss control additive, and a bridging agent that is a degradable material; forming a self-degrading filter cake comprising the bridging agent within the formation; and permitting the filter cake to self-degrade. (See, e.g., claim 15; Specification at page 3, lines 15-20). In certain embodiments, the bridging agent is present in the well drill-in and servicing fluid in an amount sufficient to create an efficient filter cake, for example, an amount of from about 0.1% to about 30% by weight. (See, e.g., claims 29 & 30; Specification at page 6, line 27 - page 7, line 10). In certain embodiments, the degradable material has a particle size distribution in the range of from about 0.1 micron to about 1.0 millimeter. (See, e.g., claim 28; Specification at page 12, lines 13-15).

Other embodiments of Appellants' invention provide well drill-in and servicing fluids. These fluids comprise: a viscosified fluid; a fluid loss control additive; and a bridging agent that is a degradable material. (See, e.g., claim 47; Specification at page 3, lines 21-23). In certain embodiments, the degradable material has a particle size distribution in the range of from about 0.1 micron to about 1.0 millimeter. (See, e.g., claim 55; Specification at page 12, lines 13-15).

VI. GROUNDS OF REJECTION TO BE REVIEWED ON APPEAL

The Examiner has rejected finally claims 15-18, 20-23, 29, 30, 47-50, 56-64, 66, and 67 under 35 U.S.C. § 102(b) as being anticipated by *Moradi-Araghi*. Appellants disagree with these rejections as improper.

The Examiner also has finally rejected claims 15, 23, 28, 47, 50, 55, and 65 under 35 U.S.C. § 103(a) as being unpatentable over *Moradi-Araghi* in view of *Dobson*, *Himes*, or *Cowan*. Appellants disagree with these rejections as improper.

² A copy of the specification as filed is provided in Appendix D to this Brief. The citations to the specification in this Brief are given by way of example, and potential support for the claimed elements is not limited to those portions of the specification cited.

VII. ARGUMENTS

- A. *Moradi-Araghi* cannot anticipate claims 15-18, 20-23, 29, 30, 47-50, 56-64, 66, and 67 because *Moradi-Araghi* does not disclose, either expressly or inherently, any degradable material bridging agent or the formation of a filter cake comprising that bridging agent.

In the Final Office Action, the Examiner rejected claims 15-18, 20-23, 29, 30, 47-50, 56-64, 66, and 67 under 35 U.S.C. § 102(b) as being anticipated by *Moradi-Araghi*. Anticipation can be established only when every element of the claim is disclosed by a single prior art reference. MANUAL OF PATENT EXAMINING PROCEDURE § 2131 (2008) (hereinafter “MPEP”); *RCA Corp. v. Applied Digital Data Systems, Inc.*, 730 F.2d 1440, 1444, 221 USPQ 385, 388 (Fed. Cir. 1984). In relying on the inherent disclosure of a reference to anticipate a claim element, the Examiner bears the burden to “provide a basis in fact and/or technical reasoning to reasonably support the determination that the allegedly inherent characteristic necessarily flows from the teachings of the applied prior art.” MPEP at § 2112 (emphasis in original); *see Ex parte Levy*, 17 USPQ2d 1461, 1464 (Bd. Pat. App. & Inter. 1990). “The fact that a certain result or characteristic may occur or be present in the prior art is not sufficient to establish the inherency of that result or characteristic. MPEP at § 2112 (emphasis in original); *see In re Rijckaert*, 9 F.3d 1531, 1534, 28 USPQ2d 1955, 1957 (Fed. Cir. 1993). However, *Moradi-Araghi* does not, either expressly or inherently, disclose the use of a bridging agent that is a degradable material, as recited in claims 15 and 47, nor does it disclose forming a self-degrading filter cake that comprises the bridging agent and allowing that filter cake to degrade, as recited in claim 15. Thus, *Moradi-Araghi* cannot anticipate the rejected claims.

Moradi-Araghi contains no discussion whatsoever of a degradable material acting as a bridging agent, which the Examiner does not dispute. Rather, *Moradi-Araghi* discloses crosslinkers encapsulated with a (poly)orthoester coating (*see Moradi-Araghi* at Abstract & col. 3, ll. 7-17), which the Examiner believes to anticipate a degradable material bridging agent. In rejecting Appellants’ claims, the Examiner assumes that because “dependent claims 22 and 49 define the degradable material (and, thus, the bridging agent) to be, *inter alia*, (poly)orthoester,” those materials in any form will “inherently” act as a bridging agent and form a self-degrading filter cake when placed downhole. (Office Action dated August 8, 2007 (“the Aug. 8, 2007 Office Action”) at 3). The Examiner has failed to and cannot establish that *Moradi-Araghi* inherently discloses these elements.

1. The Examiner has failed to meet his burden of showing that the encapsulated crosslinkers in *Moradi-Araghi* necessarily act as bridging agents and form a filter cake.

In arguing inherent disclosure, the Examiner previously hypothesized from *Moradi-Araghi* that “a thin gel may be produced [which] allows for an initial filter cake to form and degrade (at least in part) before a second type of cake is formed.” (Aug. 8, 2007 Office Action at 4). However, as Appellants noted in their response to this argument, this notion of “initial” and “second” filter cakes is unexplained by anything in *Moradi-Araghi* or elsewhere in the art. There is no explanation of how forming a gel will necessarily lead to the formation of a filter cake, much less a filter cake that comprises the degradable materials recited in *Moradi-Araghi*.

In the Final Office Action, the Examiner apparently drops this theory, but instead attempts to place the burden of disproving that *Moradi-Araghi* discloses these elements, simply maintaining that “[i]t is unclear from Applicant’s arguments … as to why Moradi-Araghi’s composition for oil field applications containing (poly)orthoester … would not function in the same manner when provided into an oil well/borehole.” (Final Office Action at 5). However, the Examiner bears the burden to prove that the crosslinking agents encapsulated with degradable materials disclosed in *Moradi-Araghi* will necessarily act as a bridging agent and form a self-degrading filter cake in a subterranean formation. MPEP at § 2112; Levy, 17 USPQ2d at 1464. The Examiner has assumed the degradable materials in *Moradi-Araghi* will act as a bridging agent simply because they comprise polymers of the same chemical structure as those in several of Appellants’ dependent claims (*i.e.*, poly(orthoesters recited in dependent claims 22 and 49)). There is no support for this assumption. The mere fact that the bridging agent of Appellants’ claims may comprise (poly)orthoesters does not indicate that the (poly)orthoester-encapsulated crosslinkers of *Moradi-Araghi* are bridging agents. These polymeric materials may be present in a number of different physical forms having various physical properties, and there is no reason to believe that the materials in *Moradi-Araghi* have the physical forms and properties required to act as bridging agents and form a filter cake. Although dependent claims 22 and 49 do recite that the degradable material may comprise one or more different polymers (*e.g.*, poly(orthoesters)), that recitation does not imply that those polymers in any form will act as a bridging agent or form a self-degrading filter cake. Rather, dependent claims incorporate the additional elements from independent claims 15 and 47, respectively, which require those steps and therefore limit

the scope of possible bridging agent materials recited in dependent claims 22 and 49. *See* 35 U.S.C. § 112 ¶ 4 (2004). *Moradi-Araghi* does not disclose or teach any material that will inherently satisfy these elements. Having failed to establish a *prima facie* case of inherent anticipation, the Examiner's rejections under § 102 should be reversed on those grounds alone.

2. The encapsulated crosslinkers in *Moradi-Araghi* cannot act as bridging agents or form a filter cake.

The encapsulated crosslinkers disclosed in *Moradi-Araghi* cannot anticipate Appellants' claims since those encapsulated crosslinkers cannot act as bridging agents or to form a self-degrading filter cake within the formation because they are not properly sized to do so, rebutting any case of inherency that the Examiner may assert. The Examiner asserts that *Moradi-Araghi* contemplates capsules of a degradable polymer that "can be fairly small" or "of small enough size to be useful as a bridging agent," citing column 4 and Example 1 of *Moradi-Araghi*. (Aug. 8, 2007 Office Action at 4). However, neither these portions of *Moradi-Araghi* nor the balance of that reference even mention the size of the particles. *Moradi-Araghi* does mention the molecular weights of certain polymers that may be used to encapsulate the crosslinkers therein (*see Moradi-Araghi* at col. 4, ll. 52-62), but this provides no information whatsoever regarding the particle size of the encapsulated crosslinkers.

Rather than explaining how any particles in *Moradi-Araghi* are properly sized to act as bridging agents, the Examiner simply conjectures that larger capsules taught in *Moradi-Araghi* can be used as bridging agents, "even if not optimally." (Aug. 8, 2007 Office Action at 4). To the contrary, it is well known and documented in the art that particles chosen without reference to the particle size needed to bridge pore throats within a subterranean formation will fail to act as a bridging agent, and will fail to form a filter cake. *See, e.g.*, Gatlin, C., and Nemir, C.E., "Some Effects of Size Distribution on Particle Bridging in Lost Circulation and Filtration Tests," JOURNAL OF PETROLEUM TECHNOLOGY at p.576 (June 1961) (Table 1: "no bridge formed and no pressure held" in simulated formations tested with randomly selected sack of medium sized particulates); Mahajan, N.C. and Barron, B.M., "Bridging Particle Size Distribution, A Key Factor in the Designing of Non-Damaging Completion Fluids," Paper SPE 8792, presented at the 4th Symposium on Formation Damage Control, Jan. 28-29, 1980, Bakersfield, Calif. (bridging on formation face "can only be done by proper selection of bridging particle sizes in relation to the formation pore sizes"); U.S. Patent No. 2,815,079 to Goins *et al.*, at col. 2, l. 56 - col. 3, l. 20 (materials having particle size distributions falling outside of a narrow range "were found ... to

fail in sealing the larger-size openings even though all of these had particles of the same maximum size").³ Rather, larger particles of degradable materials, like those in *Moradi-Araghi*, simply sit on top of the pore throats in a subterranean formation, creating new pore spaces between the formation particulates and the degradable particles. Fluid will flow through these new pore throats readily, and no filter cake will form. Thus, the larger encapsulated crosslinkers in *Moradi-Araghi* are not bridging agents, nor will they form a self-degrading filter cake.

The Final Office Action ignores these arguments and maintains that particle size is not relevant to "the rejected claims" since those claims do not recite specific particle sizes. However, all of the rejected claims do require the use of a degradable material bridging agent, as recited in claims 15 and 47 (the parent claims of all claims in the application), and claim 15 further requires forming a self-degrading filter cake that comprises that bridging agent. As Appellants have shown, because the encapsulated crosslinkers of *Moradi-Araghi* are not properly sized, they are not bridging agents and will not perform these steps.

Therefore, because *Moradi-Araghi* does not disclose these elements recited in claims 15 and 47, *Moradi-Araghi* cannot anticipate these claims, and claims 15 and 47 are allowable over *Moradi-Araghi*. Moreover, since "a claim in dependent form shall be construed to incorporate by reference all the limitations of the claim to which it refers," and since claims 16-18, 20-23, 29, 30, 48-50, 56-64, 66, and 67 depend, either directly or indirectly, from independent claim 15 or 47, these dependent claims are allowable for at least the same reasons, in addition to the reasons discussed below with respect to claim 29. *See* 35 U.S.C. § 112 ¶ 4 (2004). Accordingly, Appellants respectfully request the reversal of these rejections.

- B. *Moradi-Araghi* cannot anticipate claims 29 and 30 because, as the Examiner concedes, the degradable materials in *Moradi-Araghi* are not capable of forming an efficient filter cake.

Moreover, *Moradi-Araghi* cannot anticipate dependent claim 29, in addition to the reasons discussed above with respect to claim 15 from which claim 29 depends, because *Moradi-Araghi* does not disclose including an amount of a bridging agent sufficient to form an "efficient filter cake." The Examiner admits that larger particles in *Moradi-Araghi* may not bridge pore throats and form a filter cake "optimally" (Aug. 8, 2007 Office Action at 4), acknowledging that any filter cake formed with the particles described in *Moradi-Araghi* may not be an "efficient"

³ Copies of each of the references cited here are provided in Appendix B to this Brief.

one. Indeed, the references cited in Section A. above indicate that larger particles will not form any filter cake at all, much less an “efficient filter cake” within Appellants’ definition.

Therefore, because *Moradi-Araghi* does not disclose the additional elements recited in dependent claim 29, *Moradi-Araghi* cannot anticipate claim 29. Moreover, since “a claim in dependent form shall be construed to incorporate by reference all the limitations of the claim to which it refers,” and since claim 30 depends from claim 29, claim 30 is allowable for at least the same reason. Accordingly, Appellants respectfully request the reversal of these rejections.

- C. **No combination of *Moradi-Araghi* with *Dobson*, *Himes*, and/or *Cowan* can obviate claims 15, 23, 28, 47, 50, 55, and 65 because none of those references teaches or suggests modifying the particle size of the degradable materials in *Moradi-Araghi* to act as a bridging agent.**

In the Final Office Action, the Examiner rejected claims 15, 23, 28, 47, 50, 55, and 65 under 35 U.S.C. § 103(a) as unpatentable over *Moradi-Araghi*. In order to form a basis for a § 103(a) rejection, there must be some teaching, suggestion, or other rationale for why a person of skill in the art would modify or combine the prior art teachings to arrive at the claimed invention. MPEP at § 2141. “Rejections on obviousness cannot be sustained by mere conclusory statements; instead, there must be some articulated reasoning with some rational underpinning to support the legal conclusion of obviousness.” *Id.*; see *KSR International Co. v. Teleflex Inc.*, 550 U.S. ___, 82 USPQ2d 1385, 1396 (2007); *In re Kahn*, 441 F.3d 977, 988, 78 USPQ2d 1329, 1336 (Fed. Cir. 2006). As discussed in Section A. above, *Moradi-Araghi* does not teach the use of a bridging agent that is a degradable material, as recited in claims 15 and 47, nor does it teach forming a self-degrading filter cake that comprises the bridging agent and allowing that filter cake to degrade, as recited in claim 15. Nor does *Dobson*, *Himes*, or *Cowan* teach these elements. The Examiner also concedes that *Moradi-Araghi* does not teach any particle size distribution in the range recited in claims 28 and 55. (August 8, 2007 Office Action at 5). The Examiner has provided no such rationale for modifying *Moradi-Araghi* to include any of these missing elements. Thus, the combination of *Moradi-Araghi* with *Dobson*, *Himes*, or *Cowan* cannot obviate the rejected claims.

The Examiner concedes that *Moradi-Araghi* “is silent regarding the particle size of ... the bridging agent and the degradable polymer.” (August 8, 2007 Office Action at 5). The Final Office Action simply asserts that these particle sizes and the other elements of Appellants’

claims would be obvious modifications of *Moradi-Araghi* on the grounds that *Dobson, Himes*, and *Cowan* teach that “it is routine to alter the particle size of fluid composition additives to provide enhanced fluid loss prevention.” (Final Office Action at 7). This conclusory statement grossly mischaracterizes the teachings of those references. *Dobson, Himes*, and *Cowan* specifically deal with optimal sizes of bridging agent particulates to block pore throats in a formation, whereas the encapsulated crosslinkers of *Moradi-Araghi* are used for the entirely unrelated purpose of gelling a fluid. These additives are only related (if at all) in that they are both used in subterranean treatments. This in no way suggests that a person of skill in the art would apply specifications for the size of bridging agent particulates to improve an encapsulated crosslinker. Compare MPEP at § 2143 (use of a known technique to improve similar devices or products in the same way may be obvious).

Nor does the Examiner provide any reasonable explanation for why it would be effective or useful to modify the particle sizes of encapsulated crosslinkers, which have no ascertainable use as bridging agents or on fluid loss prevention in general, much less to modify them according to the teachings of references that speak to bridging agents. The Examiner has asserted that it would be obvious to modify the encapsulated crosslinking agents in *Moradi-Araghi* by optimizing the size of those particulates to obtain “specific degradation times,” making them suitable for use as bridging agents. (Aug. 8, 2007 Office Action at 6). However, there is no reason to believe that the particle sizes to which the crosslinking agents in *Moradi-Araghi* would be optimized in order to obtain those degradation times would coincide with the particle sizes necessary to act as a bridging agent, as Appellants’ claims require. Indeed, modifying the encapsulated crosslinking agents in *Moradi-Araghi* to make them small enough to act as a bridging agent may render them unsuitable for the very purpose taught in *Moradi-Araghi* of accomplishing delayed gelation of a fluid, for example, if the degradable encapsulating material is not big enough to encapsulate the crosslinking agent material. See MPEP at § 2143.01. Thus, it would not be obvious to modify *Moradi-Araghi* to include a bridging agent that is a degradable material, the steps of forming a self-degrading filter cake that comprises the bridging agent and allowing that filter cake to degrade, or a degradable material bridging agent having a particle size distribution in the range recited in claims 28 and 55. Thus the rejections of claims 15, 23, 28, 47, 50, 55, and 65 under § 103(a) should be reversed.

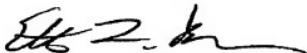
VIII. SUMMARY AND PETITION FOR A ONE-MONTH EXTENSION OF TIME TO FILE THIS BRIEF

In light of the foregoing, Appellants respectfully request that the final rejection of the pending claims should be reversed and the application be remanded for allowance of the pending claims, or, alternatively, remand the application for further examination if appropriate references can be found by the Examiner.

A Notice of Panel Decision from Pre-Appeal Review was mailed on August 19, 2008, which reset the deadline for the filing of this Brief for one month from the mailing date of that Notice. Appellants hereby petition under the provisions of 37 C.F.R. § 1.136(a) for a one-month extension of time to file this Brief, extending the deadline for filing this brief from September 19, 2008 to October 19, 2008. As October 19, 2008 fell on a Sunday, this Brief is considered timely filed with the requested extension.

The Commissioner is hereby authorized to debit Baker Botts L.L.P.'s Deposit Account No. 02-0383, Order Number 063718.0187, in the amount of \$670.00 for (1) the fee of \$130.00 under 37 C.F.R. § 1.17(a)(1) for the One-Month Petition for Extension of Time to File this Brief, and (2) the fee of \$540.00 under 37 C.F.R. § 41.20(b)(2) for filing an appeal brief. Should the Commissioner deem that any additional fees are due, including any fees for extensions of time, the Commissioner is authorized to debit Baker Botts L.L.P.'s Deposit Account No. 02-0383, Order Number 063718.0187.

Respectfully submitted,



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Date: October 20, 2008

APPENDIX A: CLAIMS INVOLVED IN APPEAL

1.- 14. (Cancelled)

15. (Previously Presented) A method of drilling an open hole in a subterranean formation, comprising the steps of:

circulating through the drill pipe and drill bit a well drill-in and servicing fluid comprising a viscosified fluid, a fluid loss control additive, and a bridging agent that is a degradable material;

forming a self-degrading filter cake comprising the bridging agent within the formation; and

permitting the filter cake to self-degrade.

16. (Original) The method of claim 15 wherein the step of forming a self-degrading filter cake comprises forming the filter cake upon the face of the formation itself, upon a sand screen, or upon a gravel pack.

17. (Original) The method of claim 15 wherein the step of permitting the filter cake to self-degrade comprises contacting the filter cake with a degrading agent for a period of time such that the bridging agent is dissolved thereby.

18. (Original) The method of claim 17 wherein the well drill-in and servicing fluid comprises the degrading agent.

19. (Cancelled)

20. (Original) The method of claim 17 wherein the degrading agent comprises water.

21. (Original) The method of claim 15 wherein the degradable material comprises a degradable polymer or a dehydrated compound.

22. (Previously Presented) The method of claim 21 wherein the degradable polymer comprises at least one degradable polymer selected from the group consisting of a polysaccharide, a chitin, a chitosan, a protein, an orthoester, an aliphatic polyester, a poly(glycolide), a poly(lactide), a poly(ϵ -caprolactone), a poly(hydroxybutyrate), a polyanhydride, an aliphatic polycarbonate, a poly(orthoester), a poly(amino acid), a poly(ethylene oxide), and a polyphosphazene.

23. (Original) The method of claim 15 wherein the degradable material comprises a plasticizer.

24. (Withdrawn) The method of claim 21 wherein the dehydrated compound comprises anhydrous sodium tetraborate or anhydrous boric acid.

25. (Withdrawn) The method of claim 15 wherein the degradable material comprises a stereoisomer of a poly(lactide).

26. (Withdrawn) The method of claim 15 wherein the degradable material comprises poly(lactic acid) and a compound chosen from the group consisting of sodium borate, boric oxide, calcium carbonate, and magnesium oxide.

27. (Withdrawn) The method of claim 26 wherein the poly(lactic acid) is present in a stoichiometric amount.

28. (Original) The method of claim 15 wherein the degradable material has a particle size distribution in the range of from about 0.1 micron to about 1.0 millimeter.

29. (Previously Presented) The method of claim 15 wherein the bridging agent is present in the well drill-in and servicing fluid in an amount sufficient to create an efficient filter cake.

30. (Previously Presented) The method of claim 29 wherein the bridging agent is present in the well drill-in and servicing fluid in an amount in the range of from about 0.1% to about 30% by weight.

31. (Withdrawn) The method of claim 15 wherein the viscosified fluid comprises a viscosifier; wherein the viscosifier is present in the well drill-in and servicing fluid in an amount in the range of from about 0.13% to about 0.16% by weight; wherein the viscosifier is xanthan; wherein the fluid loss control additive is present in the well drill-in and servicing fluid in an amount in the range of from about 1% to about 1.3% by weight; wherein the fluid loss control additive is starch; wherein the bridging agent comprising the degradable material is present in the well drill-in and servicing fluid in the range of from about 1% to about 5% by weight; and wherein the degradable material comprises poly(lactic acid) and either calcium carbonate or magnesium oxide.

32.- 46. (Cancelled)

47. (Previously Presented) A well drill-in and servicing fluid comprising:
a viscosified fluid;
a fluid loss control additive; and
a bridging agent that is a degradable material.

48. (Original) The well drill-in and servicing fluid of claim 47 wherein the degradable material comprises a degradable polymer or a dehydrated compound.

49. (Previously Presented) The well drill-in and servicing fluid of claim 48 wherein the degradable polymer comprises at least one degradable polymer selected from the group consisting of a polysaccharide, a chitin, a chitosan, a protein, an orthoester, an aliphatic polyester, a poly(glycolide), a poly(lactide), a poly(ϵ -caprolactone), a poly(hydroxybutyrate), a polyanhydride, an aliphatic polycarbonate, a poly(orthoester), a poly(amino acid), a poly(ethylene oxide), and a polyphosphazene.

50. (Original) The well drill-in and servicing fluid of claim 47 wherein the degradable material comprises a plasticizer.

51. (Withdrawn) The well drill-in and servicing fluid of claim 48 wherein the dehydrated compound comprises anhydrous sodium tetraborate or anhydrous boric acid.

52. (Withdrawn) The well drill-in and servicing fluid of claim 47 wherein the degradable material comprises a stereoisomer of a poly(lactide).

53. (Withdrawn) The well drill-in and servicing fluid of claim 47 wherein the degradable material comprises poly(lactic acid) and a compound chosen from the group consisting of sodium borate, boric oxide, calcium carbonate, and magnesium oxide.

54. (Withdrawn) The well drill-in and servicing fluid of claim 53 wherein the poly(lactic acid) is present in a stoichiometric amount.

55. (Original) The well drill-in and servicing fluid of claim 47 wherein the degradable material has a particle size distribution in the range of from about 0.1 micron to about 1.0 millimeter.

56. (Original) The well drill-in and servicing fluid of claim 47 wherein the viscosified fluid is present in the well drill-in and servicing fluid in an amount in the range of from about 68% to about 99% by weight.

57. (Original) The well drill-in and servicing fluid of claim 47 wherein the viscosified fluid comprises water, oil, or a mixture thereof.

58. (Original) The well drill-in and servicing fluid of claim 47 wherein the viscosified fluid comprises a viscosifier.

59. (Original) The well drill-in and servicing fluid of claim 58 wherein the viscosifier is present in the well drill-in and servicing fluids of the present invention in an amount sufficient to suspend the bridging agent in the well drill-in and servicing fluid for a desired period of time.

60. (Original) The well drill-in and servicing fluid of claim 58 wherein the viscosifier is present in the well drill-in and servicing fluids of the present invention in an amount in the range of from about 0.01% to about 0.6% by weight.

61. (Original) The well drill-in and servicing fluid of claim 58 wherein the viscosifier comprises a biopolymer, a cellulose derivative, guar, or a guar derivative.

62. (Original) The well drill-in and servicing fluid of claim 61 wherein the viscosifier is xanthan.

63. (Original) The well drill-in and servicing fluid of claim 47 wherein the fluid loss control additive is present in the well drill-in and servicing fluid in an amount sufficient to provide a desired degree of fluid loss control.

64. (Original) The well drill-in and servicing fluid of claim 47 wherein the fluid loss control additive is present in the well drill-in and servicing fluid in an amount in the range of from about 0.01% to about 2% by weight.

65. (Original) The well drill-in and servicing fluid of claim 47 wherein the fluid loss control additive comprises starch, starch ether derivatives, hydroxyethylcellulose, cross-linked hydroxyethylcellulose, or mixtures thereof.

66. (Previously Presented) The well drill-in and servicing fluid of claim 47 wherein the bridging agent is present in the well drill-in and servicing fluid in an amount sufficient to create a desirable number of voids in the filter cake.

67. (Previously Presented) The well drill-in and servicing fluid of claim 47 wherein the bridging agent is present in the well drill-in and servicing fluid ranging from about 0.1% to about 30% by weight.

68. (Withdrawn) The well drill-in and servicing fluid of claim 47 wherein the viscosified fluid comprises a viscosifier; wherein the viscosifier is present in the well drill-in and servicing fluids of the present invention in an amount in the range of from about 0.13% to about 0.16% by weight; wherein the viscosifier is xanthan; wherein the fluid loss control additive is present in the well drill-in and servicing fluid in an amount in the range of from about 1% to about 1.3% by weight; wherein the fluid loss control additive is starch; wherein the bridging agent comprising the degradable material is present in the well drill-in and servicing fluid in the range of from about 1% to about 5% by weight; and wherein the degradable material comprises poly(lactic acid) and either calcium carbonate or magnesium oxide.

69. - 81. (Cancelled)

APPENDIX B: EVIDENCE

Contents:

1. Gatlin, C., and Nemir, C.E., "Some Effects of Size Distribution on Particle Bridging in Lost Circulation and Filtration Tests," JOURNAL OF PETROLEUM TECHNOLOGY (June 1961).
2. Mahajan, N.C. and Barron, B.M., "Bridging Particle Size Distribution, A Key Factor in the Designing of Non-Damaging Completion Fluids," Paper SPE 8792, presented at the 4th Symposium on Formation Damage Control, Jan. 28-29, 1980, Bakersfield, Calif.
3. U.S. Patent No. 2,815,079 to Goins *et al.*

PETROLEUM TRANSACTIONS



Some Effects of Size Distribution on Particle Bridging in Lost Circulation and Filtration Tests

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INTRODUCTION

A common cure of lost circulation is the introduction of granular bridging agents into the mud system. Many materials, such as ground nut shells, are used for this purpose. If the trouble causing void (fracture, fissure, vug, etc.) is not too large, the granular agent forms a "bridge" across or within the opening. Successively smaller particles in the mud stream then accumulate on and/or within this bridge until normal filtration is finally established. The efficiency of many bridging agents has been studied in the laboratory using various slot testers.^{1,2}

Many investigators have remarked that a granular bridging material should have the proper particle size distribution. With the exception of the broad range specified in the patent of Goins and Nash,³ there is apparently no definition as to what this distribution should be.

A bridge may be initiated when several particles of lost circulation material lodge against each other in a fracture or other void. Smaller particles then may bridge the openings between the larger, previously bridged particles. This process continues until the voids become quite small and the problem becomes one of filtration. It would seem logical that an optimum particle size distribution exists, i.e., one containing the proper quantity of properly sized material to fill the successive, smaller voids of the bridge.

The filtration characteristics of drilling fluids may be subject to a similar analysis. It has been clearly demonstrated by many workers that the filtration behavior of various muds can be altered by particle size control.⁴⁻⁶ Slusser, *et al.*,⁷ divided filtration into three periods and showed that particle sizes affecting a given period did not necessarily affect other portions of the filtration curve.

An analogous problem is the proper sizing of gravel, liner slots and screen sizes in various sand-exclusion problems. Here the situation is reversed in that a proper "void" size, rather than the size of the bridging agent, is sought. The classic work of Coberly⁸ forms the

quantitative basis for most sand-exclusion processes. It is interesting to note that, in general, Coberly's work has been overlooked by most drilling-mud researchers.

Other investigators have made various studies of the effect of particle size distribution on drilling-mud properties. As a part of their studies, Fancher and Oliphant reported 30-minute filtration loss of a variety of mixtures of particle sizes.⁹ Gates and Bowie noted an effect of particle size distribution on filtration, as well as on other physical properties.⁴

MAXIMUM DENSITY THEORY

A maximum density mixture has been mentioned as the possible solution for both lost circulation and mud filtration problems.¹⁰ Furnas¹¹ derived mathematically a method for obtaining maximum density of beds of packed solids, having either a given number of component sizes or a continuous gradation of sizes. This work was verified experimentally by Anderegg.¹² For mixtures having a continuous grading of sizes, the interval between sizes is taken as successive screen sizes of interval $\sqrt{2}$. The ratio of the quantity of each size and the next smaller size is given by the equation

$$r = \frac{1}{\phi^{n/m}}$$

where r = the quantity ratio between successive sizes of interval $\sqrt{2}$,

ϕ = the porosity of a bed composed of material of one screen size,

n = one less than the number of component sizes obtained from the ordinate of Fig. 1, and

m = one less than the number of screens used, i.e., the number of size intervals of ratio $\sqrt{2}$.

Fig. 1, number of size intervals of ratio $\sqrt{2}$ taken from Furnas' paper, gives the value of $n + 1$ for any given values of ϕ and K , where K is the ratio of the diameter of the smallest particles to the diameter of the largest particles. Measurement by weight assumes, of course, constant density for all particle sizes. Choosing the quantity of the smallest particle size as a unit weight, the required weights of the successively larger intervals are then $r, r^2, r^3, \dots, (r)^m$. Thus, the grading curve of a maximum density mixture represents a geometric progression of ratio r .

*Original manuscript received in Society of Petroleum Engineers office, April 1, 1961; revised manuscript received, March 23, 1961.

¹Currently with Texaco, Inc., Sweetwater, Tex.

²References given at end of paper.

³Discussion of this and all following technical papers is invited. Discussion in writing (three copies) may be sent to the office of the *Journal of Petroleum Technology*. Any discussion offered after Dec. 31, 1961, should be in the form of a new paper. No discussion should exceed 10 per cent of the manuscript being discussed.

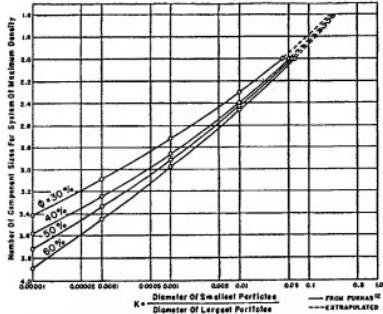


FIG. 1—RELATION BETWEEN SIZE RATIO AND NUMBER OF COMPONENT SIZES FOR SYSTEMS OF MAXIMUM DENSITY.

The purpose of this study was the preliminary application of the Furnas theory to some particle bridging features of lost circulation and mud filtration.

LOST CIRCULATION TESTS

These tests were conducted with a wedge-shaped slot tester, as described elsewhere.² The slot used had an entrance width of 0.50 in., tapering to about 0.06 in. at the exit.

A 50-lb, randomly selected sack of medium-sized crushed walnut shells was screened using United States Standard sieves; the sizes of successive sieves vary by $\sqrt{2}$. The particle size distribution of this sample is shown in Fig. 2. It is realized, of course, that not all sacks will necessarily have this distribution. The maximum density distribution of particle sizes then was calculated by Furnas' method, using $\phi = 0.50$; this distribution curve also appears in Fig. 2.

A nut shell sample having its original particle size distribution was thoroughly mixed into a 16-gal sample of mud in a concentration of 20 lb/bbl. Likewise, a quantity of particles was combined to give the calculated maximum density distribution. This was mixed into an identical portion of mud in the same concentration of 20 lb/bbl.

Each sample was pumped through the tester at about 8 gal/min until bridging occurred, or until the entire sample was expended. A stable bridge occurred when fluid did not pass the slot at 225-psi differential. Results of these tests are shown in Table 1, Runs 1 through 12. It is clear that the maximum density mixture consistently bridged the slot, while that from the original sack did not.

An additional quantity of the largest particles (12 mesh) then was added to the standard sample so that it contained the same amount of the largest size as did the maximum density sample. Runs 13 through 15 were made with this mixture. In Run 13 a stable bridge formed; however, Runs 14 and 15 were unsuccessful. These three tests suggest that, while the quantity of large particles is important in initiating the bridge, a proper distribution of successively smaller sizes supplements the "seal".

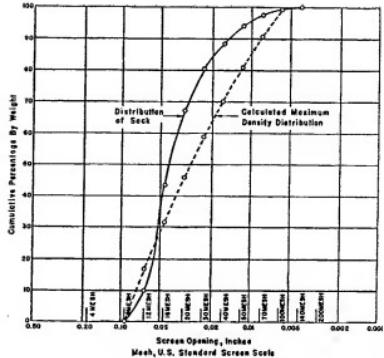


FIG. 2—PARTICLE SIZE DISTRIBUTION OF RANDOM NUT-SHELL SACK.

FILTRATION TESTS

Standard API equipment was used for the filtration tests against filter paper. Other tests substituted a 2 1/4-in. diameter by 2-in.-thick sandstone core for the filter paper. The cores used were quite uniform and had permeabilities of 600 to 800 md.

The fractionated aquagel samples obtained by Jessen and Mungan⁴ were used in this investigation. Their nomenclature will be used for each size range as listed in Table 2, taken from their paper. Muds having maximum density, as well as standard particle size distributions, were prepared as defined by the following. These will be referred to by number.

MUD

1. 6.1 per cent by weight of particles having the original size distribution of Sizes B through M.

2. 6.1 per cent by weight of the calculated maximum density distribution of Sizes B through M plus 4.23 gm of particle Size M. The extra quantity of Size M was required to furnish viscosity.

3. 4.0 per cent by weight of Size M only.

4. 6.1 per cent by weight of particles having the original distribution of Sizes H through M.

TABLE 1—RESULTS OF WEDGE-SHAPED SLOT TESTS

Run No.	Nut Shell Sample	Time for Stable Bridge (sec)	Volume of Mud Pumped Through (gal)	Remarks
1	Random Sack	—	16	No bridge formed and no pressure held on system after test. ..
2	16	..
3	16	..
4	16	..
5	Maximum Density	43	3	System held 130 psi after test.
6	95	4
7	105	5
8	10	0
9	70	4.5
10	70	4.5
11	120	8
12	135	8
13	Added 150 grams of 12-mesh size to random sack sample	45	2	System held 125 psi pressure after test
14	..	—	16	System held 55 psi pressure after test
15	..	—	16	15-psi pressure bled-off in 30 sec

TABLE 2—SIZE DISTRIBUTION OF AQUAGEL (AFTER JESSEN AND MUNGAN)¹⁴

Fraction	Size Range (microns)	Cumulative Per Cent by Weight
B	40	5.56
C	40 - 20	8.41
D	20 - 10	10.81
E	10 - 4	12.91
F	4 - 2	15.91
G	2 - 1	20.42
H	1 - 0.4	29.42
I	0.4 - 0.3	41.43
K	0.3 - 0.15	62.46
L	0.15 - 0.05	99.99
M	0.05	

TABLE 3—PROPERTIES OF MUD SAMPLES

Sample	Plastic Viscosity	Initial Gel Strength (lb/100 ft ²)	10-min Gel Strength (lb/100 ft ²)
1	25 cP	10	24
2	11.5	5	17
3	6	4	15
4	20	7	26
5	11	2	4

5. 6.1 per cent by weight of the calculated maximum density distribution of Sizes H through M.

After mixing, the flow properties of the mud samples were measured with a Fann V-G meter and are given in Table 3.

A standard filtration test was run and repeated using Sample 1. Using the same procedure, filtration tests were run on Samples 2 and 3. Sample 3 flowed freely through the filter paper without depositing a filter cake. Filtration curves were drawn for Samples 1 and 2 and are shown in Fig. 3. Since the curves become linear, for convenience only the first portion of each curve is shown.

A series of filtration tests then were performed using sandstone cores as the filter septum. Results of these tests are given in Fig. 4.

DISCUSSION OF FILTRATION STUDY

FILTER PRESS TESTS

Two things are immediately apparent from Fig. 3. First, the spurt loss of mud Sample 2 is less than that of Sample 1. A second difference is the steeper slope observed for the filtration of mud Sample 2. Since Sample 2 was composed of the calculated maximum density distribution of particle sizes, except for Size M, this result does not agree with the maximum density idea. This verifies prior work showing that the straight-line portion of filtration is controlled by the highly-hydrated small sizes,¹⁵ which evidently cannot be treated

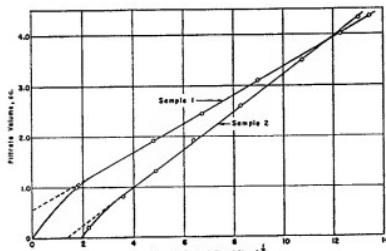


FIG. 3—FILTRATION CURVES OF SAMPLES 1 AND 2 ON FILTER PRESS.

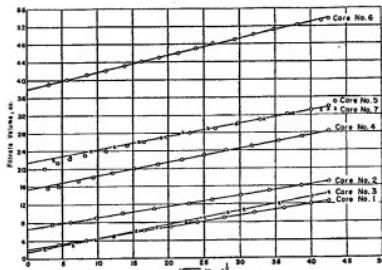


FIG. 4—FILTRATION OF MUD THROUGH SANDSTONE CORES.

as inert particles. It appears, however, that the larger sizes (which control the spurt loss) may be treated as inert particles since the maximum density mixture exhibited a reduced spurt loss on filter paper. This confirms the lost circulation results, since lost circulation is little more than a "large-scale spurt".

CORE SAMPLE TESTS

A close similarity between the curve shapes was noted in all of the core sample tests (Fig. 4). The main difference is the spurt loss, which shifts the curves vertically.

In Fig. 4, the spurt loss through Cores 1, 2 and 3 ranges from approximately 2 to 7 cc. These tests were conducted with Muds 1 and 2, containing the full range of particle sizes from B to M. Mud 2 (maximum density sample) was used on Core No. 3, and it is seen that filtration through this core had a slightly smaller spurt loss than that of mud Sample 1 through Cores 1 and 2, but had a steeper slope and, hence, a larger 30-minute water loss. This is in qualitative agreement with the previously discussed results from the filter-press experiments; however, the spurt loss difference is quite small. Slight variations in pore entry sizes of the cores may obscure the effect. The filtration tests of Samples 4 and 5 against the cores show a high spurt loss, ranging from about 15 to 38 cc. This was from two to six times as high as the spurt loss obtained from the mud samples containing the larger particles. Note from Fig. 4, however, that all the curves have substantially the same slope once bridging occurs. There was no significant difference between the filtration characteristics of mud Samples 4 and 5. Therefore, the increased spurt loss was essentially due to the deletion of the large particle sizes with a negligible contribution from the maximum density effect.

Permeability measurements were made on the core samples before and after the tests. In all cases the bulk (75 per cent or more) of formation damage occurred in the first 0.25 cm, as expected. In general, for a given particle size range, the damage depth was less for the maximum density mixture. The data were, however, scattered and inconclusive.¹⁶

SPECULATIONS

In rotary drilling, the selection of a drilling fluid often involves a considerable compromise between hole conditioning and penetration rate. Much penetration-

rate reduction has been attributed to the "chip hold-down" forces which accompany low-water-loss, high-solid-content, high-viscosity, etc., muds, even in "impermeable rocks". These forces are a consequence of a high pressure difference, or more correctly, a high pressure gradient across the hole bottom, i.e., the element being drilled.¹⁻³ It also is well known that beneath bit filtration is something quite different from that measured by the API test.⁴ Because of the continual bit action beneath bit, filtration is better described by some early portion of the filtration curve. A high spurt mud will clearly result in a reduced pressure gradient across bottom, thereby facilitating cutting removal. The use of clear water is an example.

Deletion of "large" particles from colloidal drilling muds results in high spurt muds. Once bridging occurs, however, the behavior is apparently normal. Thus, it appears possible to construct a mud which can satisfy hole-conditioning requirements with less sacrifice of drilling rate. While this is somewhat conjectural, the principle seems sound, although it is realized that continuous maintenance of such a mud may be difficult.

Many other possibilities exist for application of the Furnas theory. The selection of aggregate for gravel packs and, possibly, the sizing of particles for filtration control in other wellbore fluids are typical examples. The Furnas approach can even be applied to the packing of unconsolidated cores for laboratory purposes.

Because of the limited testing performed, the following conclusions are necessarily restricted to the few systems studied. The results are, however, sufficiently promising to encourage further work.

CONCLUSIONS

1. A maximum density distribution of nut-shell particle sizes is more efficient in bridging and sealing a wedge-shaped slot than the distribution found in a randomly selected sack.

2. A maximum density distribution of the "large" particles in commercial bentonite reduces the initial surge or "spurt loss" of a bentonite mud in the standard filter press test.

3. The maximum density theory, which is based on inert particles, apparently does not hold for the linear portion of the filtration curve of a bentonite mud.

ACKNOWLEDGMENT

The authors express their thanks to Necmettin Mungan for the use of his clay samples.

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RIDGING PARTICLE SIZE DISTRIBUTION: A KEY FACTOR IN THE DESIGNING OF NON-DAMAGING COMPLETION FLUIDS

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Inadd Company

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ABSTRACT

Great care must be exercised in the formulation and use of completion and workover fluids; otherwise extreme damage can be done by "non-damaging" fluids. Excessive loss of brines, polymers, or bridging solids to a producing strata can result in irreversible formation damage. Rapid formation of an effective filter cake on the formation face with the resultant low filtration rate and minimum solids penetration can significantly reduce the potential for formation damage.

Laboratory data indicates that low filtration rates achieved with the formation of a thin, competent filter film composed of properly sized bridging particles and hydrocolloid polymers will most effectively prevent formation damage. The deposited filter film acts as a downhole filter, screening out unwanted solids from the small volume of filtrate actually entering the formation.

INTRODUCTION

Fluids and solids invading the production zone cause formation damage. The most successful method of minimizing damage is to establish a low permeability filter film at the wellbore face as rapidly as possible. The filter film should be easily broken down when the well is put back on production. The importance of using non-damaging completion and workover fluids has long been recognized and close attention is being given to the problem in the field operations. However, some factors in designing and applying these fluids are often overlooked; the result is a "non-damaging fluid" causing formation damage. One of the critical factors in designing non-damaging fluids is obtaining surface bridging on the formation face with minimum depth solids penetration. This can only be done by proper selection of bridging particle sizes in relation to the formation pore sizes. The use of acid degradable additives in a wellbore fluid does not assure protection for a producing zone. Such additives merely make removing formation damage more practical or possible.

The most commonly used completion fluid additives are the hydroxyethyl cellulose (HEC) polymer and sized calcium carbonate bridging solids. The objective of this study was to investigate the interaction of calcium carbonate particle size distribution and hydrocolloid polymers. Previous studies have related surface bridging and particle size distribution in conventional drilling fluids. 1,2,3

Brines filtered through 2-5 micron filters are used extensively in completion and workover operations. Filtered brines are best used where formation permeability is not significantly affected by liquid invasion or where fluid loss to the formation is minimal. However, field tests have indicated the need for maintaining exceptionally clean equipment on the rig to prevent the filtered fluid from picking up rust, scale, or other debris and carrying it downhole. 4,5

The addition of properly formulated fluid loss control additives to the brine protects the formation from both solid and liquid invasion. The formation of a thin filter film on the face of the wellbore will essentially filter out all of the solids down to and including colloidal size particles. Further fluid loss is significantly reduced. The filter film then is a more effective method of solids removal than surface filters, but success with this approach depends upon the ability of the fluid to quickly establish a filter film on the formation surface.

POLYMER ADDITIVES

Certain polymers will raise the viscosity and improve the carrying capacity of water. (The polymers most commonly used in the oil fields are long chain molecules which hydrate in water -- hydrocolloids.) Other polymers will lower fluid loss when used with bridging solids. Polymers are in the colloidal size range and help in the filtration control, once the primary bridge has been established by the coarser inert bridging particles.

Core test data and field results indicate that HEC is the lesser damaging of the viscosifying

polymers most often used in the oil field.⁸ The results in Table 1 were obtained by digesting 10 g of the polymer in 700 cm³ of 15% hydrochloric acid while stirring the sample at 46 K for two hours. The solution was filtered and the residue washed, dried, and weighed. HEC has a significantly less acid insoluble residue, but if lost in excessive amounts even HEC can cause damage. Any polymer should be used in the minimum concentration that will adequately do the job; it is best to minimize polymer loss to the formation by having an effective filter film.

Besides being the least damaging polymer, HEC has other desirable fluid properties. Being a nonionic polymer, it will hydrate in all the common brines up to their saturation point including calcium bromide brine. This gives the polymer fluid system a wide viscosity range without having to resort to a high solids weighted system. Further, HEC polymer does not develop a significant gel structure under static conditions, which greatly facilitates the settling of foreign solids under static surface conditions and helps to maintain a clean system.

LIQUID LOSS CONTROL ADDITIVES

Effective fluid loss control is achieved using a combination of inert bridging solids and hydrocolloids. The formation pores are first bridged by the coarser bridging particles followed by the finer particles excessively filling up the interstitial spaces between the coarser particles to form a tightly packed layer. This stage of filter film build up is accompanied by a spurt type fluid loss during which whole fluid is lost into the formation.⁹ The fine interparticle voids in this low permeability layer are then satisfactorily bridged by the hydrocolloids. At this point, filtration, which is characterized by slow, uniform flow of fluid through the filter cake, commences. During filtration, all solids in the fluid stream are filtered on the surface of the filter film until only clear liquid invading the formation.

The volume of spurt loss is controlled by the size distribution and concentration of the inert bridging solids. The extent of bridging solid invasion into the formation pores depends upon the particle size range in relation to the pore size distribution. The maximum density distribution of particle sizes can be calculated by the method proposed by Furnas. Previous studies have looked at solid particle size distribution versus pore size distribution without hydrocolloids present. The conclusion was that the median particle size should be a third of the median pore size.⁹ A recent paper, which looked at calcium carboxylates and HEC, concluded that the one third rule might not hold.¹² Calcium carbonate bridging particles are more widely used in workover and completion operations because of their blocky shape, acid solubility, and availability in a variable size range. The presence of hydrocolloids could affect the required ratio of solid particle size distribution to pore size distribution for effective bridging. Static and dynamic filtration tests indicate starch to be a consistently effective colloid for fluid loss control.¹¹ Another widely used fluid loss control agent is calcium lignosulfonate. This paper looks at the two fluid loss control agents when used with HEC and calcium carbonate.

FILTER CAKE CLEANUP MECHANISM

The filter film formed using HEC polymer and calcium carbonate bridging particles is quite thin as compared to the conventional drilling mud filter cake. The thickness of a filter cake depends on the volume of fluid lost and on the solids concentration in the fluid. A properly formulated polymer based calcium carbonate system will form a filter film less than 0.8 mm (1/32 of an inch) in thickness. Such a film has no inherent structural strength. The filter film is supported by the formation wall so long as overbalanced conditions are maintained. When the well is swabbed or returned to production, the flow of fluids into the wellbore will mechanically break down the filter cake by flushing the carbonate particles from the pores. This cleanup mechanism is possible only when solids are stopped at the face of the wellbore. Further, the HEC polymer, which acts as mortar between the carbonate bricks, degrades with time and lowered pH. The filter film can be acidized as a remedial step. Care must be exercised in acidization since the acid will channel to the more permeable sections. A laboratory demonstration of channelling is shown in the following test using a double Hassler sleeve loaded with two Berea Sandstone cores. The cell was loaded with a high and a low permeability core and damaged with a HEC calcium carbonate fluid. After that the cores were acidized with 15% hydrochloric acid and the injectivity into the cores measured. The results are shown in Table 2. The filter cake on the high permeability core was broken down first. As a result, no acid was injected into the low permeability core. Also, acidizing can have an adverse effect on some formations. Therefore, the primary cleanup mechanism should be the natural break down of the polymer and mechanical flushing of the bridging solids. This will occur only when there is minimal indepth solids penetration.

EXPERIMENTAL PROCEDURE

The experiment involved core damage tests conducted under static conditions on high permeability Berea Sandstone cores (500 to 800 md). The first fluid samples tested were 5% salt brine containing 2.9 kg/m³ (1 ppb) HEC polymer and 10.0 kg/m³ (3.5 ppb) of calcium carbonate bridging particles. The second fluids tested were the base fluid above plus various amounts of starch and calcium lignosulfonate. All of the polymer additives degrade in a neutral or acid medium. The cores had been previously evacuated and saturated with 13% salt brine. The core permeability was measured using Solotrol (parafinic distillate) as the flow fluid phase under ambient conditions at 103 kPa (15 psi). The initial core permeability was determined with flow in one direction. Damage with the test fluid was with flow in the opposite direction at 2,068 kPa (300 psi). The fluid loss was measured. The fluid loss was not allowed to exceed one pore volume of the core (less than 7 cm³). If higher volumes were lost, the cleanup results became inconsistent. Since the purpose of these tests was to evaluate formation damage as a result of particle invasion, maintaining a constant fluid loss ensured that an equal amount of solids from each sample invaded the core. The calcium carbonate bridging particles were ground marble. Return permeability was determined with flow in the original direction. Then slices of the core were removed from the damaged

end. After each slice, the permeability of the remaining core was measured. In this manner, the depth of damage for each core was determined.

INTERPRETATION OF TEST RESULTS

In examining the core damage test data, two properties of the fluid are being evaluated. First, the ability of the test fluid to rapidly form a filter film that maintains low fluid loss and second, the ease of removal of that film.

The core damage section of the test was stopped before losing more than one pore volume (7 cm^3) of the test fluid to the core. In several instances this meant stopping in less than one minute.

Table 3 indicates about 90% cleanup for HEC polymer. The addition of starch improves the fluid loss but significantly increases formation damage.

Table 4 presents the return permeability for HEC with various size distributions of calcium carbonate bridging particles. Figure 1 shows a plot of the size distribution of the several calcium carbonates used in the tests. For CaCO₃-C, CaCO₃-D, and CaCO₃-E the return permeability did not change much with depth of the core. Product CaCO₃-D exhibited better fluid loss control than CaCO₃-C or CaCO₃-E, but the damage was fairly deep (0.64 cm). The particles size distribution of product CaCO₃-D is fairly evenly spread out between 3 to 25 microns with a median of 7.5 microns. The median for CaCO₃-C is 9.6 microns and the median for CaCO₃-E is 0.81 microns. Product CaCO₃-A, which has a similar size range but has a median size of 17 microns, had a high spurt loss. The depth of invasion was much less and the return permeability was better. Product CaCO₃-B (median size 41 microns) is too coarse to provide fluid loss control. Consequently the depth of invasion was higher than CaCO₃-A, but less than CaCO₃-C, CaCO₃-D, and CaCO₃-E. The best shut off was obtained with CaCO₃-D, but the least indepth invasion was obtained with CaCO₃-A.

Table 5 presents the return permeability results when starch or calcium lignosulfonate is added to the HEC-calcium carbonate mixtures. There was a significant improvement in fluid loss control, depth of invasion, and return permeability for all calcium carbonate samples. Product CaCO₃-D with starch in Sample b had an effective shut off but the polymer did cause some damage deep in the core. By adding calcium lignosulfonate, as in Sample c, only surface damage occurred. The best performance for fluid loss control, depth of invasion, and return permeability was with Samples c and e. Figure 3 is a plot of return permeability versus depth of the core.

Figure 2 is a plot of the typical pore size distribution for the high permeability Berea Sandstone cores used. The median pore size is 33 microns.

The testwork done here is limited in scope and additional work will have to be done to confirm the above observations. Such work needs to be conducted under dynamic conditions to simulate field conditions. The concentration of the bridging particles is also a critical factor and additional work is needed in that area.

CONCLUSION

The following are the conclusions drawn from the return permeability test work done.

- 1) A fluid that contains appropriate fluid loss control additives as well as hydroxyethyl cellulose and calcium carbonate bridging solids gives better fluid loss control with better return permeabilities than a fluid that only contains HEC and calcium carbonates.
- 2) The use of fluid loss control polymers with HEC and calcium carbonates bridging particles broadens the range of acceptable particle size distributions that will be non-damaging.
- 3) Depth of solids penetration for a properly designed fluid will be shallow.

ACKNOWLEDGEMENT

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Table 1
Acid* Solubility of Polymers

Polymer Type	Percent Residue
Xanthan Gum**	3.94
Guar Gum	5.20
Hydroxypropyl Guar (HPG)	0.82
Hydroxyethyl Cellulose (HEC)	0.08

* 15% hydrochloric acid

** Xanthan Gum had to be cooked overnight to get sufficient breakdown to obtain filtrate.

Table 2
Acidization Data on Low and High Permeability Cores

	High Permeability Core	Low Permeability Core
Initial Permeability, md	801	167
Fluid loss at 2088.4 kPa for 2 h., cm ³	16	12
15% HCl injection at 344.7 kPa for 10 min., cm ³	12	0

Table 3
Core Damage Test Data — Polymers

Fluid Sample (Concentrations in kg/m ³)	Initial Permeability** (md)	Fluid Loss (cm ³)	% of Original Permeability (Total Length of Core Cut, cm)
a 2.9 HEC	607	5.6*	94.9 (0) 88.9 (0.828) 93.4 (1.525)
b 2.9 HEC	713	5.6*	94.3 (0) 98.9 (0.506)
c 2.9 HEC + 2.9 Starch	539	5.8	37.7 (0) 47.1 (0.102) 83.1 (0.855)

* Concentrations of additives are rounded off to the nearest tenth.

* Fluid loss in less than one minute.

** Permeability values are rounded off to the nearest whole number.

Table 4
Core Damage Test Data — HEC + Carbonates

Fluid Sample‡ (Concentrations in kg/m ³)	Initial Permeability** (md)	Fluid Loss (cm ³)	% of Original Permeability (Total Length of Core Cut, cm)		
a 2.9 HEC + 10.0 CaCO ₃ — E†	576	5.2*	63.5 (0)	74.3 (0.180)	77.1 (0.704)
b 2.9 HEC + 10.0 CaCO ₃ — C†	715	11.1*	61.5 (0)	69.2 (0.142)	70.5 (0.885)
c 2.9 HEC + 10.0 CaCO ₃ — C†	496	5.6*	81.8 (0)	90.9 (0.169)	74.4 (1.048)
d 2.9 HEC + 10.0 CaCO ₃ — D†	694	5.6	58.3 (0)	65.7 (0.084)	62.8 (0.641)
e 2.9 HEC + 10.0 CaCO ₃ — D†	660	5.2	69.1 (0)	70.2 (0.124)	73.6 (0.630)
f 2.9 HEC + 10.0 CaCO ₃ — A†	585	6.2*	87.8 (0)	89.2 (0.084)	101.0 (0.858)
g 2.9 HEC + 10.0 CaCO ₃ — B†	486	5.4*	63.5 (0)	75.0 (0.191)	93.2 (1.201)
					93.4 (2.533)

‡ Concentrations of additives are rounded off to the nearest tenth.

* Fluid loss in less than one minute.

** Permeability values are rounded off to the nearest whole number.

† CaCO₃ — A, B, C, D, E — are all calcium carbonates but with different particle sizes and distribution.

Table 5
Core Damage Test Data — HEC + Carbonates + Starch/Lignosulfonate

Fluid Sample‡ (Concentrations in kg/m ³)	Initial Permeability** (md)	Fluid Loss (cm ³)	% of Original Permeability (Total Length of Core Cut, cm)	
a 2.9 HEC + 8.6 CaCO ₃ — D† + 1.4 Ca Lignosulfonate	696	5.4*	88.8 (0)	96.2 (0.140)
b 2.9 HEC + 8.6 CaCO ₃ — D† + 1.4 Starch	558	2.3	80.1 (0)	88.9 (0.154)
c 2.9 HEC + 7.1 CaCO ₃ — D† + 1.4 Starch + 1.4 Ca Lignosulfonate	551	5.2	90.0 (0)	97.0 (0.067)
d 2.9 HEC + 7.1 CaCO ₃ — C† + 1.4 Starch + 1.4 Ca Lignosulfonate	936	6.2*	69.0 (0)	83.5 (0.168)
e 2.9 HEC + 7.1 CaCO ₃ — A† + 1.4 Starch + 1.4 Ca Lignosulfonate	842	4.8	91.4 (0)	99.7 (0.126)
f 2.9 HEC + 7.1 CaCO ₃ — B† + 1.4 Starch + 1.4 Ca Lignosulfonate	809	5.6*	92.4 (0)	98.6 (0.134)

‡ Concentrations of additives are rounded off to the nearest tenth.

* Fluid loss in less than one minute.

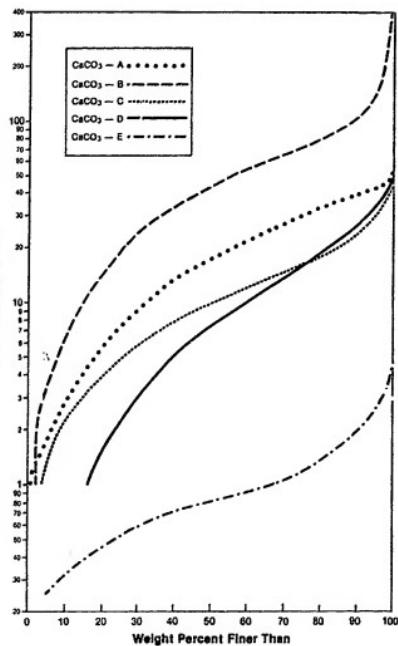


Fig. 1 - Typical particle size distribution curves.

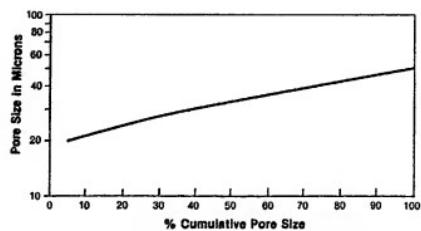


Fig. 2 - Pore size distribution of high permeability core.

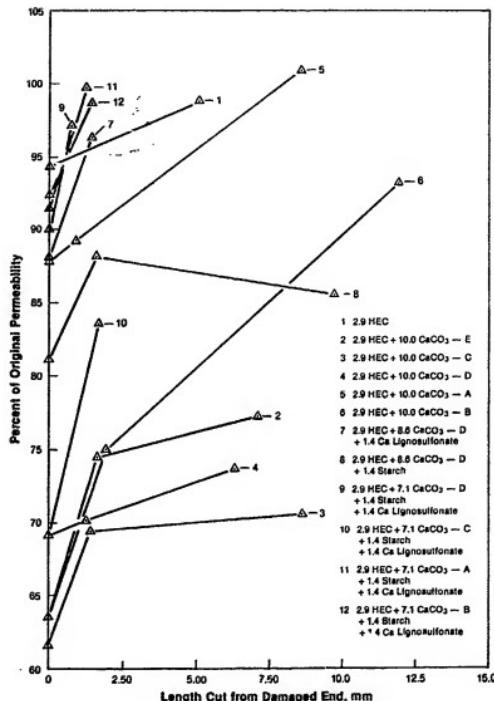


Fig. 3 - Percent of orginal permeability vs damage depth.

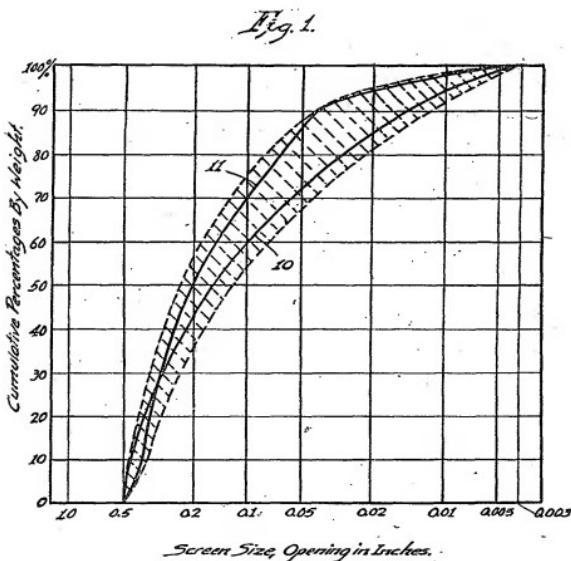
Dec. 3, 1957

W. C. GOINS, JR., ET AL
METHOD OF AND COMPOSITION FOR RECOVERING CIRCULATION
OF DRILLING FLUIDS IN WELLS

2,815,079

Filed June 29, 1954

2 Sheets-Sheet 1



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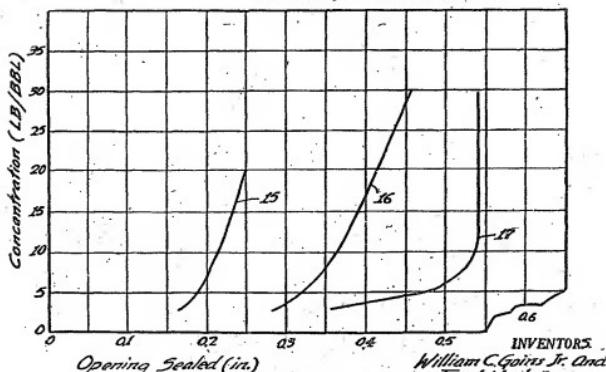
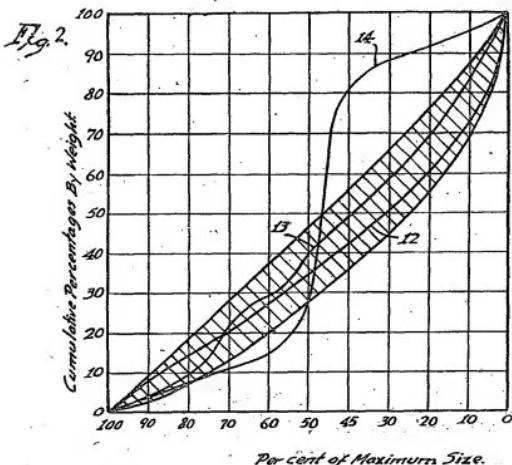
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2 Sheets-Sheet 2



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Fig. 3

METHOD OF AND COMPOSITION FOR RECOVERING CIRCULATION OF DRILLING FLUIDS IN WELLS

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Application June 29, 1954, Serial No. 440,072

9 Claims. (Cl. 166—29)

This invention relates to a method and means for preventing lost circulation of well-drilling fluids and has reference more particularly to an improved sealing material for stopping the loss of drilling fluids through formation openings during the drilling of boreholes.

In the rotary drilling of petroleum wells drilling fluids are employed which are usually composed of water, clay and, for example, barite and treating chemicals. During the drilling operation, the drilling fluid is circulated down the drill pipe, through holes in the bit, and back through the annular space between the drill pipe and the borehole to the surface. The fluid serves a number of purposes, among which are the cooling and lubrication of the pipe and bit, the flushing out of bit cuttings and the plastering of the borehole wall under a hydrostatic pressure created by the column of fluid, which plastering prevents the sloughing of loose formations and the flowing of formation fluids into the borehole. The continued circulation of the drilling fluid is, therefore, essential to the progress of the drilling operation.

It is a common experience in drilling to encounter losses of the drilling fluid through openings in the formation which may be either natural fissures, porous formations, or fissures created by well pressures. Openings which cause lost circulation must be sealed before circulation of drilling fluid can be reestablished and drilling resumed. Several methods and numerous materials have been used, therefore, to regain full circulation but no methods have been found that are successful in all cases. Most of these materials are fibrous or granular particles and are mixed with the drilling fluid in an attempt to seal off the zone of loss.

Briefly stated, our invention comprises an improved sealing material for stopping lost circulation of drilling fluids, which material consists essentially of a mixture of pre-sized hard granular particles selected from the group consisting of nut shells, synthetic resins, hard wood, and resin-impregnated wood, the said particles being compounded so that their size distribution will be substantially as follows: between 2 and 9 cumulative percent by weight retained on a screen of an opening that is 90 percent of the maximum particle size; between 12 and 28 cumulative percent by weight retained on a screen of an opening that is 70 percent of the maximum particle size; between 27 and 46 cumulative percent by weight retained on a screen of an opening that is 50 percent of the maximum particle size; between 54 and 75 cumulative percent by weight retained on a screen of an opening that is 20 percent of the maximum particle size; between 67 and 88 cumulative percent by weight retained on a screen of an opening that is 10 percent of the maximum particle size; and between 78 and 94 cumulative percent by weight retained on a screen of an opening that is 5 percent of the maximum particle size. The largest size particles will have a minimum size of at least about $\frac{1}{4}$ inch and preferably $\frac{3}{8}$ inch in any one dimension. The cumulative weight percent retained on a particular screen is obtained by adding the percent of the weight of the sample retained

on that screen to the percent of the weight of the sample retained on screens having larger openings.

More specifically, a preferred range of size distribution falling within the above defined range of invention is indicated by the following table:

TABLE I

	Percent of Maximum Particle Size	Cumulative Weight Percent Retained
10		
90		between 2 and 9.
80		between 7 and 17.
70		between 12 and 28.
60		between 20 and 37.
50		between 27 and 46.
40		between 34 and 56.
30		between 43 and 64.
20		between 54 and 75.
10		between 67 and 88.
5		between 78 and 94.
1		between 95 and 100.

20 The invention comprises also an improved sealing composition that consists essentially of a drilling fluid or mud containing a weighting agent and a liquid medium, and between 3 and 50 and preferably between 3 and 20 pounds, per barrel of drilling fluid, of a mixture of pre-sized hard granular particles selected from the group consisting of nut shells, synthetic resins, hard wood and resin-impregnated wood, having a size distribution substantially as defined above.

30 The invention further comprehends an improved method of preparing sealing material and preventing and curing lost circulation, according to which method a hard particulate or granular solid, which can be either nut shells, a synthetic resin, a hard wood, or a resin-impregnated wood is screened into its various particle sizes, and is thereafter mixed in predetermined proportions so as to provide a material of the hereinbefore defined size distribution (a screen analysis of a sample of the selected comminuted material can be made and if the comminuted material is not too far removed from the proper size distribution, portions of various screened sizes can be added to the mass of material to formulate the proper size distribution). The so-prepared sealing material is then mixed with drilling fluid containing a clay and a liquid

35 medium, usually water, the amount of sealing material being between about 3 and 50 and preferably between 3 and 20 pounds per barrel of drilling fluid. The mixture constituting the sealing composition is pumped into the well bore through the open-ended drill string, the end of the string having been set so as to direct the composition to the point of loss of circulation or fracture of the formation.

40 It is preferred to squeeze the composition into the fracture by applying pump pressure on the fluids in the borehole against closed blow-out preventers. Our method includes the step of adjusting the density of the drilling fluid employed in compounding our sealing composition, by adding weighting or thinner materials, so as to form a medium in which our sealing material will form a suitably stable suspension.

45 50 55 60 65 70 The materials above mentioned which are useful as a sealing material in the present composition and in our improved method of preventing or recovering lost circulation and regaining full returns constitute a class of materials that have sufficient strength to resist the high pressures existing in wells, have a specific gravity sufficiently close to that of the drilling fluid to minimize gravity separation of the particles, and, while hard with respect to other materials of the drilling fluid and the formation, are not abrasive to drill pipes and the like through which the material is pumped. Of the aforementioned materials, crushed nut shells and preferably walnut and hickory shells are especially suitable.

Walnut shells, for example, of the above defined size distribution were employed in drilling fluid to seal openings and they were found to seal substantially larger openings, than did other materials which were either of smaller size, softer composition or which did not exhibit the uniform and premixed size distribution of the applicants' material.

Particles of synthetic resin can be conveniently formed within the desired size range and have compressive strengths between about 20,000 and 30,000 pounds per square inch, such resins being thus well adapted to the present purposes. The specific gravity of many plastics being high they are well suited to maintaining dispersions in drilling fluids. These resins can include particles of hard rubber.

Of the various hard woods that can be employed, e. g., hickory, oak or mahogany, the denser hard woods, are preferred. The hardness and density of wood particles can be increased by impregnating the wood, preferably after comminuting it, with a synthetic resin. In this way the density of the drilling fluid can be substantially duplicated in the impregnated wood.

A preferred range which includes optimum size distributions for the selected materials is defined by the curves in the attached drawings and is as follows: a maximum size that will just pass a $\frac{1}{2}$ inch screen opening; between 5 and 20 cumulative percent by weight retained on a screen of 0.4 inch opening; between 35 and 55 cumulative percent by weight retained on a screen of 0.2 inch opening; between 54 and 75 cumulative percent by weight retained on a screen of 0.1 inch opening; between 67 and 90 cumulative percent by weight retained on a screen of 0.05 inch opening; between 80 and 95 cumulative percent by weight retained on a screen of 0.02 inch opening; between 88 and 97 cumulative percent by weight retained on a screen of 0.01 inch opening; and between 95 and 100 cumulative percent by weight retained on a screen of 0.005 inch opening.

In the accompanying drawings supplied for the purpose of illustrating the present invention,

Fig. 1 is a chart illustrating the size distribution of the particles employed in our method of recovering circulation and constituting our sealing composition, plotted cumulatively on a semi-logarithmic scale such as is customarily employed in showing particle size distribution;

Fig. 2 is a chart showing relative size distribution of the particles; and

Fig. 3 is a chart illustrating the improved test results obtained by employing our improved composition in sealing openings of indicated size.

Referring now to Fig. 1, the cross-hatched area on the chart illustrates approximately a preferred range of size distribution of particles employed in the method of our invention and constituting our sealing material. Curves 10 and 11 illustrate examples of ground walnut shells having a pre-determined composited size distribution. It is observed that the hatch-marked area is fairly narrow and that the curves 10 and 11 falling within this area define samples having that particle size distribution which will provide improved results in stopping lost circulation when employed in concentrations of between about 3 and 25 pounds per barrel of drilling fluid.

Fig. 2 illustrates the relative size distribution of the particles which constitute an essential part of our sealing composition and is applicable to any distribution falling within the range and having a maximum size at least greater than $\frac{1}{2}$ inch. The maximum particle size is expressed as that screen size through which all of the material will just pass. In plotting Fig. 2 the sizes of the various screened portions of particles of sealing material are indicated as percentages of the maximum particle size.

For example, if the maximum particle size is $\frac{1}{2}$ inch and the particle size considered is $\frac{1}{4}$ inch the percentage of maximum size will be 50 percent. This percentage of

maximum size is plotted against the cumulative percentage by weight retained on each screen employed in the analysis. It was found that the particle-size distribution effecting improved results in our composition falls within the indicated cross-hatched areas on Fig. 2. Curves 12 and 13 of this figure correspond respectively to the samples and size distributions shown by curves 10 and 11 in Fig. 1. Such size distribution is not the natural result of crushing, but is a product of recombining sizes.

5 A product having a size distribution not conforming to the distribution of our product is shown by curve 14. This material showed poor results in evaluation for recovery of circulation.

Numerous materials having size distributions falling outside of the cross-hatched areas of Figures 1 and 2 were found, upon testing as hereinafter described, to fail in sealing the larger-size openings even though all of these had particles of the same maximum size. Those failing at certain points within the areas but not remaining with 20 in the areas for all weight fractions required excessive and uneconomic proportions in drilling fluid to seal effectively the larger-size openings.

Our method and composition for stopping lost circulation in wells can best be demonstrated by laboratory apparatus since of course neither openings in the formations nor the sealing of them can be directly observed. Therefore, apparatus, hereinafter briefly described, has been devised to demonstrate numerically the superior behavior of our composition and its improved results. Sealing compositions containing walnut shells having the size distributions shown in Figures 1 and 2 were tested in the apparatus.

The test apparatus consisted primarily of a section of $\frac{1}{2}$ inch extra heavy pipe to one end of which a large 35 nitrogen bottle with regulator, hose, needle valve, bleeder, etc. is attached and to the other end of which is connected a replaceable brass plug containing slots of known length and width. Several brass plugs containing slots ranging, in 0.020 inch increments, from 0.020 to 1.020 inches in 40 width are employed with the apparatus.

In performing the test a drilling fluid containing some bentonite and barite is mixed and allowed to hydrate. After hydration numerous mixtures of the drilling fluid and different concentrations, e. g., 3, 5, 10, 15, 20, 25 and 30 pounds per barrel, of crushed walnut shells are mixed and from these samples there is determined the maximum slot that can be sealed for each concentration. The samples are each introduced into the high pressure pipe and pressures up to 1000 pounds per square inch are impressed on the mixture of drilling fluid and filler.

50 Observations are made as to the pressures required to break the seal and force drilling fluids through the slot in the brass plug and of the maximum sized openings which can be sealed up to 1000 pounds per square inch by drilling fluids containing fillers of various concentrations.

Fig. 3 illustrates the improved results obtained when employing our sealing composition. This composition is compared with other sealing compositions with unsatisfactory size distribution, although all contained some of the same maximum size particles as that of our composition. These other sealing compositions exhibited resultant poor performance. Curve 15 shows the average performance of two commercially available filler materials having an unsatisfactory size distribution. Curve 16 shows the 60 average performance of three different sealing compositions composed of crushed nut shells suspended in drilling fluid which have either a random size distribution obtained by crushing the shells and directly adding them to the drilling fluid or a size distribution outside the range prescribed for our filler particles. Curve 17 represents the results obtained when employing our sealing composition, the curve representing two series of runs with different concentrations of crushed walnut shells of two different size distributions within our disclosed range.

70 It can be seen from the curves 15, 16 and 17 of Fig. 3

that variations in the size distribution of the filler particles effect substantial differences in the ability of the sealing compositions containing the fillers to seal openings in formations. For example, curve 16 shows that a drilling fluid containing material which did not conform to the size distribution of the invention would seal openings in formations up to those of only about 0.35 inches in width. The larger sized openings, those of 0.5 inches and greater, required, in the instances where the openings could be sealed at all, excessively high concentrations of filler material of the other size distributions. It was in fact found that one sample of drilling fluid containing random sized particles would seal openings of as great a width as that of the composition of invention, but three times the weight of filler material was required to do this.

Curve 17 of Fig. 3 which shows substantially identical results obtained from two series of tests of our sealing composition containing from about 3 pounds of crushed walnut shells per barrel up to 30 pounds per barrel shows that increasing the concentration from 3 to 5 pounds per barrel rapidly increases the size of opening that can be sealed and that no apparent improvement is obtained after about 10 pounds per barrel was used.

In the introduction of our graded materials in drilling fluid into the borehole it will usually be found necessary first to remove the drill (unless the holes in the drill are large enough for passage of the largest particles of filler material) and to employ special conveying and pumping apparatus adapted to handling relatively large size filler material. It may be more convenient to maintain this equipment on service trucks and apply it to the surface apparatus of wells only when the well is being treated to correct a lost circulation problem. It was found that the quantity of drilling fluid containing filler material that is required to seal a formation can be substantially reduced by first determining the point of lost circulation in the borehole by such methods as that disclosed in the copending application of Martin and Wyckoff, Ser. No. 359,358, filed June 3, 1953, now Patent 2,773,236 December 4, 1956, and thereafter releasing the drilling fluid at or near the point of lost circulation. The general procedure for introducing fluid into the well to seal formation openings and apparatus for introducing the fluid is described in the copending application Ser. No. 255,442, filed November 8, 1951 of Goins and others, now abandoned.

Employment of our graded filling material in the successful correction of lost circulation and recovery of complete circulation in a well is described in the following specific example in which the foregoing laboratory findings are confirmed and the beneficial results obtainable only from our specially sized material are amply demonstrated.

In the drilling of a well with an 8 1/4 inch diameter bit, a 9 1/2 inch casing having been set at about 8900 feet, lost circulation first occurred in the well while drilling at about 9200 feet with a lime treated mud having a density of 16.1 pounds per gallon. Fine mica was added to the drilling mud and the circulation loss was temporarily halted. The drilling was then continued to a depth of 9400 feet when a loss of circulation again occurred. The drill was then pulled back into the casing and circulation was attempted at 250 pounds per square inch pump pressure. After a subsequent period of three hours, it was found that 100 percent circulation still could not be obtained.

Remedial measures were thereupon employed to stem the loss in circulation. The drilling string was withdrawn and the bit removed; the pipe was then run back open ended to about 9200 feet. The well was again tested but still did not show 100 percent circulation. A filler material comprising walnut hulls and having a size distribution outside of the range disclosed for our material was mixed with 120 barrels of drilling mud in the amount of 19.2 pounds of filler per barrel of mud. This

suspension was pumped into the well until about 30 barrels had been displaced down the drill pipe and into the annular space and an additional 90 barrels were in the drill pipe. This placed the mud containing filler material above the casing seat. The blowout preventer was then closed and the suspension was slowly squeezed into the formation by pumping. A maximum pressure of only 10 pounds per square inch could be obtained during the squeezing operation even after 90 barrels of the suspension had been pumped into the formation. The drill pipe was then pulled to the casing and the well was allowed to set for six hours. The treatment did not restore circulation.

Crushed walnut hulls which had been screened and separated in various screen sizes and reconstituted to provide a material having a size distribution falling within the range of the present invention as shown, for example, by the crosshatched area of Fig. 1, were then mixed with 115 barrels of drilling mud in the proportion of 13 pounds of graded walnut shells per barrel of drilling mud. The suspension of walnut hulls in the drilling mud was stabilized by adding as a thickener of the mud approximately one pound of polyacrylonitrile for each 60 pounds of walnut shells. An 18 inch displacement pump, with screen removed, was employed to drive the drilling mud containing the filling material into the well. The suspension was displaced down the well until about 30 barrels of the material was in the annular space thus placing some of the material above the casing seat. This, in itself, restored 100 percent circulation but, to prevent a recurrence of the loss, a squeeze operation was employed. At the beginning of the squeeze the annular pressure rose with slow pumping to 350 p. s. i. and when the pump was shut off this fell to 320 p. s. i. With a drilling mud of 16.0 pounds per gallon density in the hole at the time, this placed the equivalent of a 16.7 pounds per gallon mud at the point of loss. After a wait of a few minutes, slow pumping at about 8 strokes per minute was resumed and for a short period of about 5 minutes the well took mud at 320 p. s. i., at which time our hull suspension sealed the formation and the pressure then climbed rapidly to 315 p. s. i. The pressure bled to 500 p. s. i. and then held steady. When pumping was resumed the pressure built rapidly to 580 p. s. i. and held, with no bleed off. This pressure, added to hydrostatic pressure, gave the equivalent of a mud of 17.2 pounds per gallon density. The total amount of the sealing composition, containing our walnut-hull sealing material, displaced into the formation was 10 barrels. The pipe was then pulled to the casing, 250 p. s. i. pressure was reimposed and the well was allowed to set for 3 hours. The hole was then circulated in stages to bottom. Drilling was resumed with no further loss of fluid at the sealed formation.

Our sealing composition which essentially contains the graded sealing material of hereindefined size will usually comprise water and a clay but the sealing material can also be mixed with a non-aqueous drilling fluid such as an oil-base mud. The composition can also comprise one or more fibrous filler materials.

Having described our invention, we claim:

1. A sealing material for addition to drilling fluids for preventing and curing lost circulation, the said material comprising hard granular particles selected from the group consisting of nut shells, synthetic resins, hard wood, and resin impregnated wood, containing particles of maximum size that are at least about 1/4 inch in any one dimension, and having a compounded size distribution such that between 2 and 9 cumulative percent by weight is retained on a screen of an opening that is 90 percent of the maximum particle size, between 12 and 28 cumulative percent by weight is retained on a screen of an opening that is 70 percent of the maximum particle size, between 27 and 46 cumulative percent by weight is retained on a screen of an opening that is 50 percent of the maximum

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particles size, between 54 and 75 cumulative percent by weight is retained on a screen of an opening that is 20 percent of the maximum particle size, between 67 and 88 cumulative percent by weight is retained on a screen of an opening that is 10 percent of the maximum particle size, and between 78 and 94 cumulative percent by weight is retained on an opening that is 5 percent of the maximum particle size, said sealing material having been prepared by separating particles according to their size and then combining particles of different size in proportions to give a mixture having the particle size distribution defined herein.

2. The sealing material of claim 1 in which the selected hard granular particles consist of comminuted nut shells.

3. The material of claim 2 in which the selected hard granular particles consist of comminuted walnut shells.

4. A sealing material for addition to drilling fluids for preventing and curing lost circulation, the said material comprising hard granular particles selected from the group consisting of nut shells, synthetic resins, hard wood, and resin impregnated wood, containing particles of maximum size that will just pass through a screen of 0.5 inch opening, and having a compounded size distribution substantially as follows: between 5 and 20 cumulative percent by weight retained on a screen of 0.4 inch opening; between 35 and 55 cumulative percent by weight retained on a screen of 0.2 inch opening; between 54 and 75 cumulative percent by weight retained on a screen of 0.1 inch opening; between 67 and 90 cumulative percent by weight retained on a screen of 0.05 inch opening; between 80 and 95 cumulative percent by weight retained on a screen of 0.02 inch opening; between 88 and 97 cumulative percent by weight retained on a screen of 0.01 inch opening; and between 95 and 100 cumulative percent by weight retained on a screen of 0.005 inch opening, said sealing material having been prepared by separating particles according to their size and then combining particles of different size in proportions to give a mixture having the particle size distribution defined herein.

5. The sealing material of claim 4 in which the selected hard granular particles consist of comminuted nut shells.

6. The sealing material of claim 4 in which the selected hard granular particles consist of comminuted walnut shells.

7. A method of preparing a sealing material for restoring the circulation of well-drilling fluids lost through openings or fractures in formations through which the borehole of the well passes, the said method comprising: separating, according to size, particles of a hard granular material selected from the group consisting of nut shells, synthetic resins, hard wood, and resin impregnated wood; and mixing together predetermined proportions by weight of the separated particles of different size so as to obtain a composited mixture having a size distribution in which the particles of maximum size are at least about $\frac{1}{4}$ inch in any one dimension, between 2 and 9 cumulative percent by weight is retained on a screen of an opening that is 90 percent of the maximum particle size, between 12 and 28 cumulative percent by weight is retained on a screen of an opening that is 70 percent of the maximum particle size, between 27 and 46 cumulative percent by weight is retained on a screen of an opening that is 50 percent of the maximum particle size, between 54 and 75 cumulative percent by weight is retained on a screen of an opening that is 20 percent of the maximum particle size, between 67 and 88 cumulative percent by weight is retained on a screen of an opening that is 10 percent of the maximum particle size, and between 78 and 94 cumulative percent by weight is retained on a screen of an opening that is 5 percent of the maximum particle size, and be-

tween 78 and 94 cumulative percent by weight is retained on an opening that is 5 percent of the maximum particle size.

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8. A sealing composition consisting essentially of a drilling fluid containing a weighting agent, a liquid medium, and between 3 and 50 pounds per barrel of drilling fluid, of pre-sized hard granular particles selected from the group consisting of nut shells, synthetic resins, hard wood and resin-impregnated wood, the selected particles having a maximum size of at least $\frac{1}{4}$ inch and a size distribution such that between 2 and 9 cumulative percent by weight is retained on a screen of an opening that is 90 percent of the maximum particle size; between 12 and 28 cumulative percent by weight is retained on a screen of an opening that is 70 percent of the maximum particle size; between 27 and 46 cumulative percent by weight is retained on a screen of an opening that is 50 percent of the maximum particle size; between 54 and 75 cumulative percent by weight is retained on a screen of an opening that is 20 percent of the maximum particle size; between 67 and 88 cumulative percent by weight is retained on a screen of an opening that is 10 percent of the maximum particle size; and between 78 and 94 cumulative percent by weight is retained on an opening 20 that is 5 percent of the maximum particle size, said hard granular particles having been prepared by separating particles according to their size and then combining particles of different size in proportions to give a mixture having the particle size distribution defined herein.

9. A method of combating lost circulation of drilling fluid in wells by sealing openings or fractures in the penetrated formations, the said method comprising introducing into the borehole of a well and conducting by means of pressure applied thereto to the point of lost circulation 35 a sealing composition consisting essentially of a drilling fluid containing a weighting agent and a liquid medium and between 3 and 50 pounds per barrel of drilling fluid of a mixture of pre-sized hard granular particles selected from the group consisting of nut shells, synthetic resins, hard wood and resin-impregnated wood, containing particles of maximum size that are at least about $\frac{1}{4}$ inch in any one dimension, and having a compounded size distribution such that between 2 and 9 cumulative percent by weight is retained on a screen of an opening that is 90 percent of the maximum particle size, between 12 and 28 cumulative percent by weight is retained on a screen of an opening that is 70 percent of the maximum particle size, between 27 and 46 cumulative percent by weight is retained on a screen of an opening that is 50 percent of the maximum particle size, between 54 and 75 cumulative percent by weight is retained on a screen of an opening that is 20 percent of the maximum particle size, between 67 and 88 cumulative percent by weight is retained on a screen of an opening that is 10 percent of the maximum particle size, and between 78 and 94 cumulative percent by weight is retained on an opening that is 5 percent of the maximum particle size, said hard granular particles having been prepared by separating particles according to their size and then combining particles of different size in proportions to give a mixture having the particle size distribution defined herein.

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APPENDIX C: RELATED PROCEEDINGS

None

APPENDIX D: SPECIFICATION AS FILED

IMPROVED SUBTERRANEAN TREATMENT FLUIDS AND METHODS OF TREATING SUBTERRANEAN FORMATIONS

BACKGROUND OF THE INVENTION

1. Field of the Invention.

[0001] The present invention relates to bridging agents for use in subterranean formations, to well drill-in and servicing fluids comprising such bridging agents, and to methods of using such bridging agents and well drill-in and servicing fluids in subterranean drilling operations.

2. Description of Related Art

[0002] Often, once drilling of a well bore in a subterranean formation has been initiated, an operator will employ a fluid referred to as a "well drill-in and servicing fluid." As referred to herein, the term "well drill-in and servicing fluid" will be understood to mean a fluid placed in a subterranean formation from which production has been, is being, or may be cultivated. For example, an operator may begin drilling a subterranean borehole using a drilling fluid, cease drilling at a depth just above that of a productive formation, circulate a sufficient quantity of a well drill-in and servicing fluid through the bore hole to completely flush out the drilling fluid, then proceed to drill into the desired formation using the well drill-in and servicing fluid. Well drill-in and servicing fluids are often utilized, *inter alia*, to minimize damage to the permeability of such formations.

[0003] Well drill-in and servicing fluids may also include "fluid loss control fluids." As referred to herein, the term "fluid loss control fluid" will be understood to mean a fluid designed to form a filter cake onto a screen or gravel pack, or in some cases, directly onto the formation. For example, a fluid loss control fluid may comprise a comparatively small volume of fluid designed to form a filter cake so as to plug off a "thief zone" (a formation, most commonly encountered during drilling operations, into which the drilling fluid may be lost). Generally, well drill-in and servicing fluids are designed to form a fast and efficient filter cake on the walls of the well bores within the producing formations to minimize leak-off and damage. The filter cake is removed before hydrocarbons from the formation are produced. Conventionally, removal has been by contacting the filter cake with one or more subsequent fluids.

[0004] Other conventional methods of removing the filter cake include formulating the well drill-in and servicing fluid so as to include an acid-soluble particulate solid bridging agent. The resultant filter cake formed by such well drill-in and servicing fluid is then contacted with a strong acid to ultimately dissolve the bridging agent. This method is problematic, however, because the strong acid often corrodes metallic surfaces and completion equipment such as sand control screens, thereby causing such equipment to prematurely fail. Further, the acid may damage the producing formation. Additionally, the acid may cause the bridging agent to dissolve too quickly, resulting in the acid being lost into the formation, rather than completely covering the filter cake.

[0005] Another method has been to use a water-soluble particulate solid bridging agent in the well drill-in and servicing fluid, which is later contacted with an aqueous salt solution that is undersaturated with respect to such bridging agents. This method is problematic, however, because such bridging agents may require a relatively long period of time to dissolve in the solutions, due to, *inter alia*, the presence of various gelling agents in the well drill-in and servicing fluids. Such gelling agents shield the water-soluble bridging agents. A further problem is that the aqueous salt solution has a limited range of possible densities.

SUMMARY OF THE INVENTION

[0006] The present invention relates to bridging agents for use in subterranean formations, to well drill-in and servicing fluids comprising such bridging agents, and to methods of using such bridging agents and well drill-in and servicing fluids in subterranean drilling operations.

[0007] An example of a method of the present invention comprises the steps of: placing a well drill-in and servicing fluid in a subterranean formation, the well drill-in and servicing fluid comprising a viscosifier, a fluid loss control additive, and a bridging agent comprising a degradable material; and forming a self-degrading filter cake comprising the bridging agent upon a surface within the formation whereby fluid loss to the formation through the self-degrading filter cake is reduced.

[0008] Another example of a method of the present invention comprises a method of degrading a filter cake in a subterranean formation, the filter cake having been deposited therein by a well drill-in and servicing fluid comprising a bridging agent, comprising the step of utilizing a bridging agent comprising a degradable material.

[0009] Another example of a method of the present invention comprises a method of drilling an open hole in a subterranean formation, comprising the steps of: circulating through a drill pipe and drill bit a well drill-in and servicing fluid comprising a viscosified fluid, a fluid loss control additive, and a bridging agent comprising a degradable material; forming a filter cake comprising the bridging agent upon a surface within the formation; and permitting the filter cake to degrade.

[0010] An example of a composition of the present invention is a well drill-in and servicing fluid comprising a viscosified fluid; a fluid loss control additive; and a bridging agent comprising a degradable material.

[0011] The features and advantages of the present invention will be readily apparent to those skilled in the art upon a reading of the description of the preferred embodiments, which follows.

BRIEF DESCRIPTION OF THE DRAWINGS

[0012] Figure 1 depicts a graphical representation of the results of a dynamic filtration test performed on seven exemplary embodiments of filter cakes formed from well drill-in and servicing fluids of the present invention.

[0013] Figure 2 depicts a graphical representation of the results of a break test performed on seven exemplary embodiments of filter cakes formed from well drill-in and servicing fluids of the present invention.

DESCRIPTION OF PREFERRED EMBODIMENTS

[0014] The present invention relates to bridging agents for use in subterranean formations, to well drill-in and servicing fluids comprising such bridging agents, and to methods of using such bridging agents and well drill-in and servicing fluids in subterranean drilling operations.

[0015] The well drill-in and servicing fluids of the present invention generally comprise a viscosified fluid comprising a viscosifier, a fluid loss control additive, and a bridging agent comprising a degradable material capable of undergoing an irreversible degradation downhole. The term "irreversible" as used herein means that the degradable material once degraded should not recrystallize or reconsolidate while downhole, e.g., the degradable material should degrade *in situ* but should not recrystallize or reconsolidate *in situ*. The terms "degradation" or "degradable" refer to both the two relatively extreme cases of hydrolytic degradation that the degradable material may undergo, *i.e.*, heterogeneous (or bulk erosion) and homogeneous (or surface erosion), and any stage of degradation in between these two. This degradation can be a result of, *inter alia*, a chemical or thermal reaction or a reaction induced by radiation.

[0016] A variety of viscosified fluids may be included in the well drill-in and servicing fluids of the present invention. These are fluids whose viscosities have been enhanced by the use of a viscosifier. In certain embodiments, the viscosified fluid may comprise a base fluid such as water, oil, or mixtures thereof. The viscosified fluid is present in the well drill-in and servicing fluids of the present invention in an amount in the range of from about 68% to about 99% by weight. In certain preferred embodiments, the viscosified fluid is present in the well drill-in and servicing fluids of the present invention in an amount in the range of from about 90% to about 97% by weight.

[0017] The viscosified fluids comprise a viscosifier. A variety of viscosifiers may be included in the well drill-in and servicing fluids of the present invention. Examples of suitable viscosifiers include, *inter alia*, biopolymers such as xanthan and succinoglycan, cellulose derivatives such as hydroxyethylcellulose and guar and its derivatives such as hydroxypropyl guar. In certain preferred embodiments, the viscosifier is xanthan. The viscosifier is present in the well drill-in and servicing fluids of the present invention in an amount sufficient to suspend the bridging agent and drill cuttings in the well drill-in and

servicing fluid. More particularly, the viscosifier is present in the well drill-in and servicing fluids of the present invention in an amount in the range of from about 0.01% to about 0.6% by weight. In certain preferred embodiments, the viscosifier is present in the well drill-in and servicing fluid in an amount in the range of from about 0.13% to about 0.30% by weight.

[0018] The well drill-in and servicing fluids of the present invention further comprise a fluid loss control additive. A variety of fluid loss control additives can be included in the well drill-in and servicing fluids of the present invention, including, *inter alia*, starch, starch ether derivatives, hydroxyethylcellulose, cross-linked hydroxyethylcellulose, and mixtures thereof. In certain preferred embodiments, the fluid loss control additive is starch. The fluid loss control additive is present in the well drill-in and servicing fluids of the present invention in an amount sufficient to provide a desired degree of fluid loss control. More particularly, the fluid loss control additive is present in the well drill-in and servicing fluid in an amount in the range of from about 0.01% to about 3% by weight. In certain preferred embodiments, the fluid loss control additive is present in the well drill-in and servicing fluid in an amount in the range of from about 1% to about 2% by weight.

[0019] The well drill-in and servicing fluids of the present invention further comprise a bridging agent comprising a degradable material. The bridging agent becomes suspended in the well drill-in and servicing fluid and, as the well drill-in and servicing fluid begins to form a filter cake within the subterranean formation, the bridging agent becomes distributed throughout the resulting filter cake, most preferably uniformly. In certain preferred embodiments, the filter cake forms upon the face of the formation itself, upon a sand screen, or upon a gravel pack. After the requisite time period dictated by the characteristics of the particular degradable material utilized, the degradable material undergoes an irreversible degradation. This degradation, in effect, causes the degradable material to substantially be removed from the filter cake. As a result, voids are created in the filter cake. Removal of the degradable material from the filter cake allows produced fluids to flow more freely.

[0020] Generally, the bridging agent comprising the degradable material is present in the well drill-in and servicing fluid in an amount sufficient to create an efficient filter cake. As referred to herein, the term "efficient filter cake" will be understood to mean a filter cake comprising no material beyond that required to provide a desired level of fluid loss control. In certain embodiments, the bridging agent comprising the degradable material is present in the

well drill-in and servicing fluid in an amount ranging from about 0.1% to about 32% by weight. In certain preferred embodiments, the bridging agent comprising the degradable material is present in the well drill-in and servicing fluid in the range of from about 3% and about 10% by weight. In certain preferred embodiments, the bridging agent is present in the well drill-in and servicing fluids in an amount sufficient to provide a fluid loss of less than about 15 mL in tests conducted according to the procedures set forth by API Recommended Practice (RP) 13. One of ordinary skill in the art with the benefit of this disclosure will recognize an optimum concentration of degradable material that provides desirable values in terms of enhanced ease of removal of the filter cake at the desired time without undermining the stability of the filter cake during its period of intended use.

[0021] Nonlimiting examples of suitable degradable materials that may be used in conjunction with the present invention include but are not limited to degradable polymers, dehydrated compounds, and/or mixtures of the two. In choosing the appropriate degradable material, one should consider the degradation products that will result. Also, these degradation products should not adversely affect other operations or components. For example, a boric acid derivative may not be included as a degradable material in the well drill-in and servicing fluids of the present invention where such fluids utilize xanthan as the viscosifier, because boric acid and xanthan are generally incompatible. One of ordinary skill in the art, with the benefit of this disclosure, will be able to recognize when potential components of the well drill-in and servicing fluids of the present invention would be incompatible or would produce degradation products that would adversely affect other operations or components.

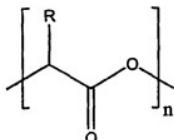
[0022] As for degradable polymers, a polymer is considered to be "degradable" herein if the degradation is due to, *inter alia*, chemical and/or radical process such as hydrolysis, oxidation, enzymatic degradation, or UV radiation. The degradability of a polymer depends at least in part on its backbone structure. For instance, the presence of hydrolyzable and/or oxidizable linkages in the backbone often yields a material that will degrade as described herein. The rates at which such polymers degrade are dependent on the type of repetitive unit, composition, sequence, length, molecular geometry, molecular weight, morphology (*e.g.*, crystallinity, size of spherulites, and orientation), hydrophilicity, hydrophobicity, surface area, and additives. Also, the environment to which the polymer is subjected may affect how the

polymer degrades, e.g., temperature, presence of moisture, oxygen, microorganisms, enzymes, pH, and the like.

[0023] Suitable examples of degradable polymers that may be used in accordance with the present invention include but are not limited to those described in the publication of *Advances in Polymer Science*, Vol. 157 entitled "Degradable Aliphatic Polyesters" edited by A.C. Albertsson. Specific examples include homopolymers, random, block, graft, and star- and hyper-branched aliphatic polyesters. Such suitable polymers may be prepared by polycondensation reactions, ring-opening polymerizations, free radical polymerizations, anionic polymerizations, carbocationic polymerizations, and coordinative ring-opening polymerization for, e.g., lactones, and any other suitable process. Specific examples of suitable polymers include polysaccharides such as dextran or cellulose; chitin; chitosan; proteins; orthoesters; aliphatic polyesters; poly(lactide); poly(glycolide); poly(ϵ -caprolactone); poly(hydroxybutyrate); poly(anhydrides); aliphatic polycarbonates; poly(orthoesters); poly(amino acids); poly(ethylene oxide); and polyphosphazenes. Of these suitable polymers, aliphatic polyesters and polyanhydrides are preferred.

[0024] Aliphatic polyesters degrade chemically, *inter alia*, by hydrolytic cleavage. Hydrolysis can be catalyzed by either acids or bases. Generally, during the hydrolysis, carboxylic end groups are formed during chain scission, and this may enhance the rate of further hydrolysis. This mechanism is known in the art as "autocatalysis," and is thought to make polymer matrices more bulk eroding.

[0025] Suitable aliphatic polyesters have the general formula of repeating units shown below:

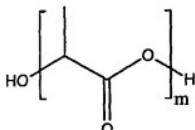


formula I

where n is an integer between 75 and 10,000 and R is selected from the group consisting of hydrogen, alkyl, aryl, alkylaryl, acetyl, heteroatoms, and mixtures thereof. Of the suitable aliphatic polyesters, poly(lactide) is preferred. Poly(lactide) is synthesized either from lactic acid by a condensation reaction or more commonly by ring-opening polymerization of cyclic lactide

monomer. Since both lactic acid and lactide can achieve the same repeating unit, the general term poly(lactic acid) as used herein refers to writ of formula I without any limitation as to how the polymer was made such as from lactides, lactic acid, or oligomers, and without reference to the degree of polymerization or level of plasticization.

[0026] The lactide monomer exists generally in three different forms: two stereoisomers L- and D-lactide and racemic D,L-lactide (*meso*-lactide). The oligomers of lactic acid, and oligomers of lactide are defined by the formula:

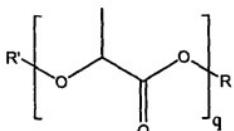


formula II

where m is an integer: $2 \leq m \leq 75$. Preferably m is an integer: $2 \leq m \leq 10$. These limits correspond to number average molecular weights below about 5,400 and below about 720, respectively. The chirality of the lactide units provides a means to adjust, *inter alia*, degradation rates, as well as physical and mechanical properties. Poly(L-lactide), for instance, is a semicrystalline polymer with a relatively slow hydrolysis rate. This could be desirable in applications of the present invention where a slower degradation of the degradable material is desired. Poly(D,L-lactide) may be a more amorphous polymer with a resultant faster hydrolysis rate. This may be suitable for other applications where a more rapid degradation may be appropriate. The stereoisomers of lactic acid may be used individually or combined in accordance with the present invention. Additionally, they may be copolymerized with, for example, glycolide or other monomers like ε-caprolactone, 1,5-dioxepan-2-one, trimethylene carbonate, or other suitable monomers to obtain polymers with different properties or degradation times. Additionally, the lactic acid stereoisomers can be modified by blending high and low molecular weight polylactide or by blending polylactide with other polyesters.

[0027] Plasticizers may be present in the polymeric degradable materials of the present invention. The plasticizers may be present in an amount sufficient to provide the desired characteristics, for example, (a) more effective compatibilization of the melt blend components, (b) improved processing characteristics during the blending and processing steps, and (c) control and regulation of the sensitivity and degradation of the polymer by moisture. Suitable

plasticizers include but are not limited to derivatives of oligomeric lactic acid, selected from the group defined by the formula:



formula III

where R is a hydrogen, alkyl, aryl, alkylaryl, acetyl, heteroatom, or a mixture thereof and R is saturated, where R' is a hydrogen, alkyl, aryl, alkylaryl, acetyl, heteroatom, or a mixture thereof and R' is saturated, where R and R' cannot both be hydrogen, where q is an integer: $2 \leq q \leq 75$; and mixtures thereof. Preferably q is an integer; $2 \leq q \leq 10$. As used herein the term "derivatives of oligomeric lactic acid" includes derivatives of oligomeric lactide.

[0028] Aliphatic polyesters useful in the present invention may be prepared by substantially any of the conventionally known manufacturing methods such as those described in U.S. Patent Nos. 6,323,307; 5,216,050; 4,387,769; 3,912,692; and 2,703,316, the relevant disclosures of which are incorporated herein by reference. In addition to the other qualities above, the plasticizers may enhance the degradation rate of the degradable polymeric materials.

[0029] Polyanhydrides are another type of particularly suitable degradable polymer useful in the present invention. Polyanhydride hydrolysis proceeds, *inter alia*, via free carboxylic acid chain-ends to yield carboxylic acids as final degradation products. The erosion time can be varied over a broad range of changes in the polymer backbone. Examples of suitable polyanhydrides include poly(adipic anhydride), poly(suberic anhydride), poly(sebacic anhydride), and poly(dodecanedioic anhydride). Other suitable examples include but are not limited to poly(maleic anhydride) and poly(benzoic anhydride).

[0030] The physical properties of degradable polymers depend on several factors such as the composition of the repeat units, flexibility of the chain, presence of polar groups, molecular mass, degree of branching, crystallinity, orientation, etc. For example, short chain branches reduce the degree of crystallinity of polymers while long chain branches lower the melt viscosity and impart, *inter alia*, elongational viscosity with tension-stiffening behavior. The properties of the material utilized can be further tailored by blending, and copolymerizing it with another polymer, or by changing the macromolecular architecture (*e.g.*, hyper-branched

polymers, star-shaped, or dendrimers, etc.). The properties of any such suitable degradable polymers (e.g., hydrophobicity, hydrophilicity, rate of degradation, etc.) can be tailored by introducing select functional groups along the polymer chains. For example, poly(phenyllactide) will degrade at about 1/5th of the rate of racemic poly(lactide) at a pH of 7.4 at 55°C. One of ordinary skill in the art with the benefit of this disclosure will be able to determine the appropriate functional groups to introduce to the polymer chains to achieve the desired physical properties of the degradable polymers.

[0031] Dehydrated compounds may be used in accordance with the present invention as a degradable material. A dehydrated compound is suitable for use in the present invention if it will degrade over time as it is rehydrated. For example, a particulate solid anhydrous borate material that degrades over time may be suitable. Specific examples of particulate solid anhydrous borate materials that may be used include but are not limited to anhydrous sodium tetraborate (also known as anhydrous borax), and anhydrous boric acid. These anhydrous borate materials are only slightly soluble in water. However, with time and heat in a subterranean environment, the anhydrous borate materials react with the surrounding aqueous fluid and are hydrated. The resulting hydrated borate materials are substantially soluble in water as compared to anhydrous borate materials and as a result degrade in the aqueous fluid. In some instances, the total time required for the anhydrous borate materials to degrade in an aqueous fluid is in the range of from about 8 hours to about 72 hours depending upon the temperature of the subterranean zone in which they are placed.

[0032] Blends of certain degradable materials may also be suitable. One example of a suitable blend of materials is a mixture of poly(lactic acid) and sodium borate where the mixing of an acid and base could result in a neutral solution where this is desirable. Another example would include a blend of poly(lactic acid) and boric oxide, a blend of calcium carbonate and poly(lactic) acid, a blend of magnesium oxide and poly(lactic) acid, and the like. In certain preferred embodiments, the degradable material is calcium carbonate plus poly(lactic) acid. Where a mixture including poly(lactic) acid is used, in certain preferred embodiments the poly(lactic) acid is present in the mixture in a stoichiometric amount, e.g., where a mixture of calcium carbonate and poly(lactic) acid is used, the mixture comprises two poly(lactic) acid units for each calcium carbonate unit. Other blends that undergo an irreversible degradation may also be suitable, if the products of the degradation do not undesirably interfere with either the

conductivity of the filter cake or with the production of any of the fluids from the subterranean formation.

[0033] The choice of degradable material can depend, at least in part, on the conditions of the well, e.g., well bore temperature. For instance, lactides have been found to be suitable for lower temperature wells, including those within the range of about 60°F to about 150°F, and polylactides have been found to be suitable for well bore temperatures above this range. Dehydrated salts may also be suitable for higher temperature wells.

[0034] Also, we have found that a preferable result is achieved if the degradable material degrades slowly over time as opposed to instantaneously. The slow degradation of the degradable material helps, *inter alia*, to maintain the stability of the filter cake.

[0035] The specific features of the degradable material may be modified so as to maintain the filter cake's filtering capability when the filter cake is intact while easing the removal of the filter cake when such removal becomes desirable. In certain embodiments, the degradable material has a particle size distribution in the range of from about 0.1 micron to about 1.0 millimeters. Whichever degradable material is utilized, the bridging agents may have any shape, including but not limited to particles having the physical shape of platelets, shavings, flakes, ribbons, rods, strips, spheroids, toroids, pellets, tablets, or any other physical shape. One of ordinary skill in the art with the benefit of this disclosure will recognize the specific degradable material and the preferred size and shape for a given application.

[0036] The filter cake formed by the well drill-in and servicing fluids of the present invention is removed after a desired amount of time by being contacted with a degrading agent. In certain embodiments, the degrading agent comprises water. The source of the degrading agent may be, *inter alia*, a well drill-in and servicing fluid, such as a gravel pack fluid or a completion brine, for instance. In certain embodiments, the source of the degrading agent may be the bridging agent itself. For example, the bridging agent may comprise a water-containing compound. Any compound containing releasable water may be used as the water-containing compound. As referred to herein, the term "releasable water" will be understood to mean water that may be released under desired downhole conditions, including, *inter alia*, temperature. In certain embodiments, the water-containing compound may be sodium acetate trihydrate, sodium borate decahydrate, sodium carbonate decahydrate, or the like. In certain preferred embodiments, the water-containing compound is sodium acetate trihydrate.

[0037] The filter cake formed by the well drill-in and servicing fluids of the present invention is a "self-degrading" filter cake. As referred to herein, the term "self-degrading filter cake" will be understood to mean a filter cake that may be removed without the need to circulate a separate "clean up" solution or "breaker" through the well bore, such clean up solution or breaker having no purpose other than to degrade the filter cake. Though the filter cakes formed by the well drill-in and servicing fluids of the present invention constitute "self-degrading" filter cakes, an operator may nevertheless occasionally elect to circulate a separate clean up solution through the well bore under certain circumstances, such as when the operator desires to hasten the rate of degradation of the filter cake. In certain embodiments, the bridging agents of the present invention are sufficiently acid-degradable as to be removed by such treatment.

[0038] An example of a method of the present invention comprises the steps of: placing a well drill-in and servicing fluid in a subterranean formation, the well drill-in and servicing fluid comprising a viscosifier, a fluid loss control additive, and a bridging agent comprising a degradable material; and forming a self-degrading filter cake comprising the bridging agent upon a surface within the formation whereby fluid loss to the formation through the self-degrading filter cake is reduced. Another example of a method of the present invention comprises a method of degrading a filter cake in a subterranean formation, the filter cake having been deposited therein by a well drill-in and servicing fluid comprising a bridging agent, comprising the step of utilizing a bridging agent comprising a degradable material.

[0039] Another example of a method of the present invention comprises a method of drilling an open hole in a subterranean formation, comprising the steps of: circulating through a drill pipe and drill bit a well drill-in and servicing fluid comprising a viscosified fluid, a fluid loss control additive, and a bridging agent comprising a degradable material; forming a filter cake comprising the bridging agent upon a surface within the formation; and permitting the filter cake to degrade.

[0040] An example of a well drill-in and servicing fluid of the present invention comprises a viscosified fluid, a fluid loss control additive, and a bridging agent comprising a degradable material.

[0041] To facilitate a better understanding of the present invention, the following examples of exemplary embodiments are given. In no way should such examples be read to limit the scope of the invention.

EXAMPLE 1

[0042] A dynamic filtration test was conducted, in a Fann Model 90B dynamic filtration tester, in which seven embodiments of filter cakes of the present invention were constructed. For each of the seven embodiments, a sample composition was formulated comprising 336 mL of a 10% aqueous solution of sodium chloride by weight, to which 0.85 grams of clarified liquid xanthan biopolymer, 7.4 grams of a non-ionic starch derivative, 20 grams of powdered polylactic acid, and 30 grams of calcium carbonate were added. This sample composition was then hot rolled for 16 hours at 150° F.

[0043] The dynamic filtration test comprised constructing filter cakes on the inner diameter of a synthetic core comprising "ALOXITETM" having a 35 micron pore throat size. The filter cakes were constructed by continuously shearing each sample composition inside the core for an hour while applying a differential pressure of 500 psid, during which time the filter cake formed on the core's inner diameter. The porous nature of the core provides the potential for fluid to leak outward in a radial direction, with the filtrate rate and volume being dependent on the integrity of the filter cake deposited on the core. The volume of filtrate for a particular sample composition was collected and recorded with time. The test concluded after 60 minutes. The results are depicted in Table 1 below, and in Figure 1.

TABLE I

Time (minutes)	Total Filtrate Volume (mL)						
	Sample Composition 1	Sample Composition 2	Sample Composition 3	Sample Composition 4	Sample Composition 5	Sample Composition 6	Sample Composition 7
0	0	0	0	0	0	0	0
10	5.64	6.20	6.14	5.33	5.42	5.68	6.33
20	6.92	7.45	7.45	6.62	6.74	6.86	7.66
30	7.84	8.48	8.53	7.72	7.79	7.88	8.83
40	8.70	9.32	9.44	8.65	8.76	8.76	9.76
50	9.56	10.11	10.24	9.55	9.62	9.58	10.63
60	10.26	10.8	11.03	10.34	10.35	10.36	11.44

[0044] The above example demonstrates, *inter alia*, that the well drill-in and servicing fluids of the present invention may be used to provide filter cakes having acceptable filtration leak off, as well as that the integrity of such filter cakes is generally repeatable over a series of tests.

EXAMPLE 2

[0045] The seven sample filter cakes prepared in Example 1 were then each subjected to a break test, in which a 10% aqueous solution of sodium chloride by weight was injected into the core at 50 psi differential pressure. Break tests for Sample Compositions 1, 2, 4, and 6 were conducted at 200°F, while break tests for Sample Compositions 3, 5 and 7 were performed at 180°F. As the sodium chloride solution began to break down each filter cake, the amount of filtrate (*e.g.*, the amount of broken filter cake) was collected and measured. The break test continued until such time as the maximum filtrate volume (50 mL) of a particular sample was collected in the Model 90B dynamic filtration tester. The results are illustrated in Table 2 below and in Figure 2.

TABLE 2

Total Filtrate Volume (mL)	Time (hrs)						
	Sample Composition 1	Sample Composition 2	Sample Composition 3	Sample Composition 4	Sample Composition 5	Sample Composition 6	Sample Composition 7
0	0	0	0	0	0	0	0
5	1.71	2.25	2.25	2.07	1.45	1.51	1.59
10	3.59	5.06	5.28	4.11	3.49	2.66	3.07
15	5.39	7.64	7.13	5.82	5.43	3.53	4.52
20	6.73	9.97	8.90	6.41	7.36	4.65	5.29
25	7.06	11.48	10.7	7.1	9.0	4.84	5.63
30	7.30	12.30	12.27	7.57	9.61	4.9	5.87
35	7.65	12.84	13.47	7.75	10.03	4.97	6.08
40	7.93	13.31	14.38	7.89	10.36	5.03	6.13

[0046] The above example illustrates, *inter alia*, that exemplary embodiments of filter cakes formed from the well drill-in and treatment fluids of the present invention are degradable.

[0047] Therefore, the present invention is well adapted to carry out the objects and attain the ends and advantages mentioned as well as those that are inherent therein. While numerous changes may be made by those skilled in the art, such changes are encompassed within the spirit of this invention as defined by the appended claims.

We claim:

1. A method for forming a self-degrading filter cake in a subterranean formation, comprising the steps of:

 placing a well drill-in and servicing fluid in a subterranean formation, the well drill-in and servicing fluid comprising a viscosified fluid, a fluid loss control additive, and a bridging agent comprising a degradable material; and

 forming a self-degrading filter cake comprising the bridging agent within the formation.

2. The method of claim 1 wherein the step of forming a self-degrading filter cake within the formation comprises forming the filter cake upon the face of the formation itself, upon a sand screen, or upon a gravel pack.

3. The method of claim 1 wherein the degradable material comprises a degradable polymer or a dehydrated compound.

4. The method of claim 3 wherein the degradable polymer comprises polysaccharides, chitins, chitosans, proteins, orthoesters, aliphatic polyesters, poly(glycolides), poly(lactides), poly(ϵ -caprolactones), poly(hydroxybutyrate), polyanhydrides, aliphatic polycarbonates, poly(orthoesters), poly(amino acids), poly(ethylene oxides), or polyphosphazenes.

5. The method of claim 1 wherein the degradable material further comprises a plasticizer or a stereoisomer of a poly(lactide).

6. The method of claim 3 wherein the dehydrated compound comprises anhydrous sodium tetraborate or anhydrous boric acid.

7. The method of claim 1 wherein the degradable material comprises poly(lactic acid) and a compound chosen from the group consisting of sodium borate, boric oxide, calcium carbonate, and magnesium oxide.

8. The method of claim 7 wherein the poly(lactic acid) is present in the degradable material in a stoichiometric amount.

9. The method of claim 1 wherein the bridging agent comprising the degradable material is present in the well drill-in and servicing fluid in an amount sufficient to create an efficient filter cake.

10. The method of claim 1 wherein the bridging agent comprising the degradable material is present in the well drill-in and servicing fluid in an amount sufficient to provide a fluid loss of less than about 15 mL per API Recommended Practice 13.

11. The method of claim 1 wherein the degradable material has a particle size distribution in the range of from about 0.1 micron to about 1.0 millimeter.

12. The method of claim 1 wherein the bridging agent comprising the degradable material is present in the well drill-in and servicing fluid in an amount in the range of from about 0.1% to about 30% by weight.

13. The method of claim 1 wherein the viscosified fluid comprises a viscosifier.

14. The method of claim 1 wherein the viscosified fluid comprises a viscosifier; wherein the viscosifier is present in the well drill-in and servicing fluid in an amount in the range of from about 0.13% to about 0.16% by weight; wherein the viscosifier is xanthan; wherein the fluid loss control additive is present in the well drill-in and servicing fluid in an amount in the range of from about 1% to about 1.3% by weight; wherein the fluid loss control additive is starch; wherein the bridging agent comprising the degradable material is present in the well drill-in and servicing fluid in the range of from about 1% to about 5% by weight; and wherein the degradable material comprises poly(lactic acid) and either calcium carbonate or magnesium oxide.

15. A method of drilling an open hole in a subterranean formation, comprising the steps of:

circulating through the drill pipe and drill bit a well drill-in and servicing fluid comprising a viscosified fluid, a fluid loss control additive, and a bridging agent comprising a degradable material;

forming a self-degrading filter cake comprising the bridging agent within the formation; and

permitting the filter cake to self-degrade.

16. The method of claim 15 wherein the step of forming a self-degrading filter cake comprises forming the filter cake upon the face of the formation itself, upon a sand screen, or upon a gravel pack.

17. The method of claim 15 wherein the step of permitting the filter cake to self-degrade comprises contacting the filter cake with a degrading agent for a period of time such that the bridging agent is dissolved thereby.

18. The method of claim 17 wherein the well drill-in and servicing fluid comprises the degrading agent.

19. The method of claim 17 wherein the bridging agent comprises the degrading agent.

20. The method of claim 17 wherein the degrading agent comprises water.

21. The method of claim 15 wherein the degradable material comprises a degradable polymer or a dehydrated compound.

22. The method of claim 21 wherein the degradable polymer comprises polysaccharides, chitins, chitosans, proteins, orthoesters, aliphatic polyesters, poly(glycolides), poly(lactides), poly(ϵ -caprolactones), poly(hydroxybutyrate), polyanhydrides, aliphatic polycarbonates, poly(orthoesters), poly(amino acids), poly(ethylene oxides), or polyphosphazenes.

23. The method of claim 15 wherein the degradable material comprises a plasticizer.

24. The method of claim 21 wherein the dehydrated compound comprises anhydrous sodium tetraborate or anhydrous boric acid.

25. The method of claim 15 wherein the degradable material comprises a stereoisomer of a poly(lactide).

26. The method of claim 15 wherein the degradable material comprises poly(lactic acid) and a compound chosen from the group consisting of sodium borate, boric oxide, calcium carbonate, and magnesium oxide.

27. The method of claim 26 wherein the poly(lactic acid) is present in a stoichiometric amount.

28. The method of claim 15 wherein the degradable material has a particle size distribution in the range of from about 0.1 micron to about 1.0 millimeter.

29. The method of claim 15 wherein the bridging agent comprising the degradable material is present in the well drill-in and servicing fluid in an amount sufficient to create an efficient filter cake.

30. The method of claim 29 wherein the bridging agent comprising the degradable material is present in the well drill-in and servicing fluid in an amount in the range of from about 0.1% to about 30% by weight.

31. The method of claim 15 wherein the viscosified fluid comprises a viscosifier; wherein the viscosifier is present in the well drill-in and servicing fluid in an amount in the range of from about 0.13% to about 0.16% by weight; wherein the viscosifier is xanthan; wherein the fluid loss control additive is present in the well drill-in and servicing fluid in an amount in the range of from about 1% to about 1.3% by weight; wherein the fluid loss control additive is starch; wherein the bridging agent comprising the degradable material is present in the well drill-in and servicing fluid in the range of from about 1% to about 5% by weight; and wherein the degradable material comprises poly(lactic acid) and either calcium carbonate or magnesium oxide.

32. A method of degrading a filter cake in a subterranean formation, the filter cake having been deposited therein by a well drill-in and servicing fluid comprising a bridging agent, comprising the step of:

utilizing a bridging agent comprising a degradable material; and

contacting the degradable material with a degrading agent for a period of time such that the degradable material is dissolved thereby.

33. The method of claim 32 wherein the bridging agent comprises the degrading agent.

34. The method of claim 32 wherein the degrading agent is supplied by a well drill-in and servicing fluid.

35. The method of claim 32 wherein the degrading agent comprises water.

36. The method of claim 32 wherein the degradable material comprises a degradable polymer or a dehydrated compound.

37. The method of claim 36 wherein the degradable polymer comprises polysaccharides, chitins, chitosans, proteins, orthoesters, aliphatic polyesters, poly(glycolides), poly(lactides), poly(ϵ -caprolactones), poly(hydroxybutyrate), polyanhydrides, aliphatic polycarbonates, poly(orthoesters), poly(amino acids), poly(ethylene oxides), or polyphosphazenes.

38. The method of claim 32 wherein the degradable material further comprises a plasticizer.

39. The method of claim 36 wherein the dehydrated compound comprises anhydrous sodium tetraborate or anhydrous boric acid.

40. The method of claim 32 wherein the degradable material comprises a stereoisomer of a poly(lactide).

41. The method of claim 32 wherein the degradable material comprises poly(lactic acid) and a compound chosen from the group consisting of sodium borate, boric oxide, calcium carbonate, and magnesium oxide.

42. The method of claim 41 wherein the poly(lactic acid) is present in the degradable material in a stoichiometric amount.

43. The method of claim 32 wherein the degradable material has a particle size distribution in the range of from about 0.1 micron to about 1.0 millimeter.

44. The method of claim 32 wherein the bridging agent comprising the degradable material is present in the well drill-in and servicing fluid in an amount sufficient to create a desirable number of voids in the filter cake.

45. The method of claim 44 wherein the bridging agent comprising the degradable material is present in the well drill-in and servicing fluid in an amount of about 0.1% to about 30% by weight.

46. The method of claim 32 wherein the well drill-in and servicing fluid comprises a viscosified fluid and a fluid loss control additive; wherein the viscosified fluid comprises a viscosifier; wherein the viscosifier is present in the well drill-in and servicing fluid in an amount in the range of from about 0.13% to about 0.16% by weight; wherein the viscosifier is xanthan; wherein the fluid loss control additive is present in the well drill-in and servicing fluid in an amount in the range of from about 1% to about 1.3% by weight; wherein the fluid loss control additive is starch; wherein the bridging agent comprising the degradable material is present in the well drill-in and servicing fluid in the range of from about 1% to about 5% by weight; and wherein the degradable material comprises poly(lactic acid) and either calcium carbonate or magnesium oxide.

47. A well drill-in and servicing fluid comprising:
 - a viscosified fluid;
 - a fluid loss control additive; and
 - a bridging agent comprising a degradable material.
48. The well drill-in and servicing fluid of claim 47 wherein the degradable material comprises a degradable polymer or a dehydrated compound.
49. The well drill-in and servicing fluid of claim 48 wherein the degradable polymer comprises polysaccharides, chitins, chitosans, proteins, orthoesters, aliphatic polyesters, poly(glycolides), poly(lactides), poly(ϵ -caprolactones), poly(hydroxybutyrate), polyanhydrides, aliphatic polycarbonates, poly(orthoesters), poly(amino acids), poly(ethylene oxides), or polyphosphazenes.
50. The well drill-in and servicing fluid of claim 47 wherein the degradable material comprises a plasticizer.
51. The well drill-in and servicing fluid of claim 48 wherein the dehydrated compound comprises anhydrous sodium tetraborate or anhydrous boric acid.
52. The well drill-in and servicing fluid of claim 47 wherein the degradable material comprises a stereoisomer of a poly(lactide).
53. The well drill-in and servicing fluid of claim 47 wherein the degradable material comprises poly(lactic acid) and a compound chosen from the group consisting of sodium borate, boric oxide, calcium carbonate, and magnesium oxide.
54. The well drill-in and servicing fluid of claim 53 wherein the poly(lactic acid) is present in a stoichiometric amount.
55. The well drill-in and servicing fluid of claim 47 wherein the degradable material has a particle size distribution in the range of from about 0.1 micron to about 1.0 millimeter.
56. The well drill-in and servicing fluid of claim 47 wherein the viscosified fluid is present in the well drill-in and servicing fluid in an amount in the range of from about 68% to about 99% by weight.
57. The well drill-in and servicing fluid of claim 47 wherein the viscosified fluid comprises water, oil, or a mixture thereof.
58. The well drill-in and servicing fluid of claim 47 wherein the viscosified fluid comprises a viscosifier.

59. The well drill-in and servicing fluid of claim 58 wherein the viscosifier is present in the well drill-in and servicing fluids of the present invention in an amount sufficient to suspend the bridging agent in the well drill-in and servicing fluid for a desired period of time.

60. The well drill-in and servicing fluid of claim 58 wherein the viscosifier is present in the well drill-in and servicing fluids of the present invention in an amount in the range of from about 0.01% to about 0.6% by weight.

61. The well drill-in and servicing fluid of claim 58 wherein the viscosifier comprises a biopolymer, a cellulose derivative, guar, or a guar derivative.

62. The well drill-in and servicing fluid of claim 61 wherein the viscosifier is xanthan.

63. The well drill-in and servicing fluid of claim 47 wherein the fluid loss control additive is present in the well drill-in and servicing fluid in an amount sufficient to provide a desired degree of fluid loss control.

64. The well drill-in and servicing fluid of claim 47 wherein the fluid loss control additive is present in the well drill-in and servicing fluid in an amount in the range of from about 0.01% to about 2% by weight.

65. The well drill-in and servicing fluid of claim 47 wherein the fluid loss control additive comprises starch, starch ether derivatives, hydroxyethylcellulose, cross-linked hydroxyethylcellulose, or mixtures thereof.

66. The well drill-in and servicing fluid of claim 47 wherein the bridging agent comprising the degradable material is present in the well drill-in and servicing fluid in an amount sufficient to create a desirable number of voids in the filter cake.

67. The well drill-in and servicing fluid of claim 47 wherein the bridging agent comprising the degradable material is present in the well drill-in and servicing fluid ranging from about 0.1% to about 30% by weight.

68. The well drill-in and servicing fluid of claim 47 wherein the viscosified fluid comprises a viscosifier; wherein the viscosifier is present in the well drill-in and servicing fluids of the present invention in an amount in the range of from about 0.13% to about 0.16% by weight; wherein the viscosifier is xanthan; wherein the fluid loss control additive is present in the well drill-in and servicing fluid in an amount in the range of from about 1% to about 1.3% by weight; wherein the fluid loss control additive is starch; wherein the bridging agent comprising

the degradable material is present in the well drill-in and servicing fluid in the range of from about 1% to about 5% by weight; and wherein the degradable material comprises poly(lactic acid) and either calcium carbonate or magnesium oxide.

69. A bridging agent comprising a degradable material.
70. The bridging agent of claim 69 wherein the degradable material comprises a degradable polymer or a dehydrated compound.
71. The bridging agent of claim 70 wherein the degradable polymer comprises polysaccharides, chitins, chitosans, proteins, orthoesters, aliphatic polyesters, poly(glycolides), poly(lactides), poly(ϵ -caprolactones), poly(hydroxybutyrate), polyanhydrides, aliphatic polycarbonates, poly(orthoesters), poly(amino acids), poly(ethylene oxides), or polyphosphazenes.
72. The bridging agent of claim 69 wherein the degradable material further comprises a plasticizer.
73. The bridging agent of claim 70 wherein the dehydrated compound comprises anhydrous sodium tetraborate or anhydrous boric acid.
74. The bridging agent of claim 69 wherein the degradable material comprises a stereoisomer of a poly(lactide).
75. The bridging agent of claim 69 wherein the degradable material comprises poly(lactic acid) and a compound chosen from the group consisting of sodium borate, boric oxide, calcium carbonate, and magnesium oxide.
76. The bridging agent of claim 75 wherein the poly(lactic acid) is present in the degradable material in a stoichiometric amount.
77. The bridging agent of claim 69 wherein the degradable material has a particle size distribution in the range of from about 0.1 micron to about 1.0 millimeter.
78. The bridging agent of claim 69 further comprising a degrading agent.
79. The bridging agent of claim 78 wherein the degrading agent comprises a source of releasable water.
80. The bridging agent of claim 79 wherein the degrading agent comprises sodium acetate trihydrate, sodium borate decahydrate, sodium carbonate decahydrate, or a mixture thereof.
81. The bridging agent of claim 78 wherein the degrading agent is present in a stoichiometric amount.

**IMPROVED SUBTERRANEAN TREATMENT FLUIDS AND METHODS OF
TREATING SUBTERRANEAN FORMATIONS**

ABSTRACT

[0001] The present invention relates to bridging agents for use in subterranean formations, to well drill-in and servicing fluids comprising such bridging agents, and to methods of using such bridging agents and well drill-in and servicing fluids in subterranean drilling operations. An example of a well drill-in and servicing fluid of the present invention comprises a viscosified fluid, a fluid loss control additive, and a bridging agent comprising a degradable material.

FIGURE 1

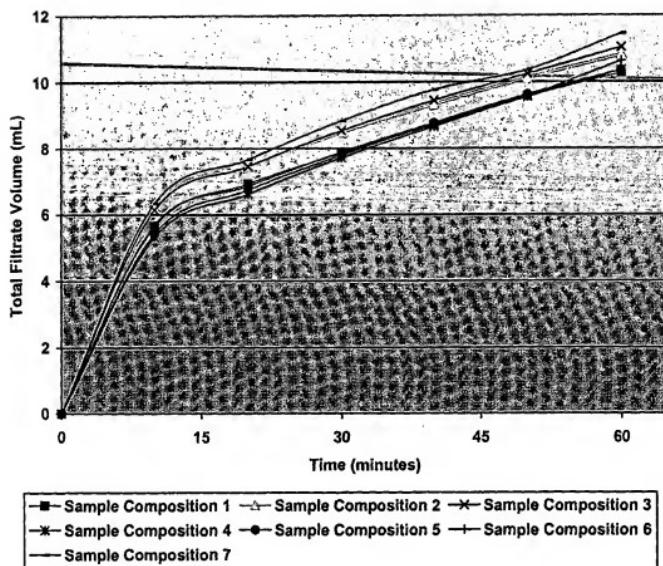
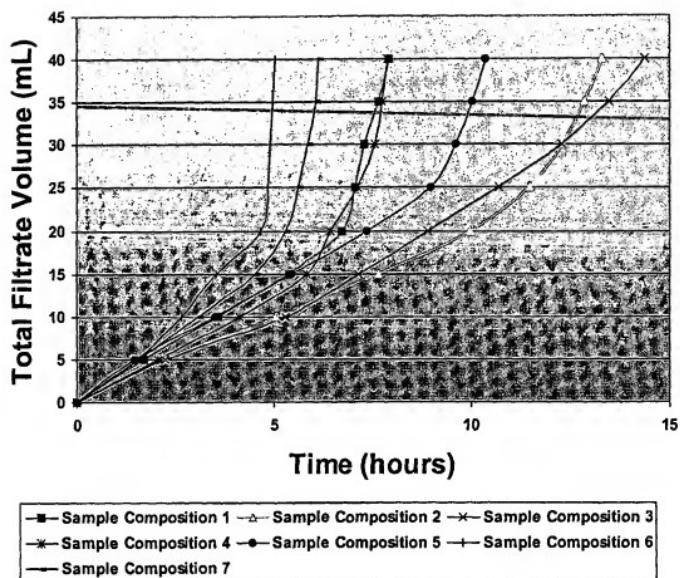


FIGURE 2



APPENDIX E: U.S. PATENT NO. 6,387,986 TO MORADI-ARAGHI *ET AL.*
(“MORADI-ARAGHI”)

(12) **United States Patent**
Moradi-Araghi et al.

(10) **Patent No.:** US 6,387,986 B1
(45) **Date of Patent:** May 14, 2002

(54) **COMPOSITIONS AND PROCESSES FOR OIL FIELD APPLICATIONS**

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523/132; 523/210; 166/300; 166/308

(58) Field of Search 523/130, 131,
523/132, 210, 211; 166/300, 308

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(57) **ABSTRACT**

Encapsulated crosslinking agents and gel-forming compositions are provided that can be utilized in oil field applications. Processes for producing said encapsulated crosslinking agents and said gel-forming compositions are also provided. In addition, a process for injecting said gel-forming composition into a subterranean formation is also provided.

22 Claims, No Drawings

**COMPOSITIONS AND PROCESSES FOR OIL
FIELD APPLICATIONS**

FIELD OF INVENTION

This invention relates to compositions and processes for oil field applications. More specifically, this invention relates to encapsulated crosslinking agents, gel-forming compositions, and processes for producing and using encapsulated crosslinking agents and gel-forming compositions.

BACKGROUND OF THE INVENTION

It is well known to those skilled in the art that certain polymers are useful in enhanced oil recovery and other oil field operations. These polymers have been used to alter the permeability of subterranean formations. For example, these polymers can be used to enhance the efficiency of water flooding, or carbon dioxide injection in enhanced oil recovery processes, to plug fractures or channels, to prevent loss of drilling fluids, and to block gas release during drilling.

Generally, these polymers are combined with a gelling agent in a liquid to form a gel-forming composition. These gel-forming compositions can be injected into a subterranean formation. These gel-forming compositions then gel in the regions of the subterranean formation that have the highest water permeability.

However, many of these polymers can gel within minutes, which makes the application of said gel-forming compositions less useful in many oil field applications. This is because these gel-forming compositions cannot be properly placed in a subterranean formation, prior to it forming a gel.

Various methods have been tried to slow down gel formation, however, slower gel formation is needed because this will allow placement of gel-forming compositions in subterranean formations prior to forming a gel, especially in hostile environments.

Therefore, there is a need in the oil industry for a gel-forming composition with a slower gel formation rate (also known as "gelation rate").

SUMMARY OF THE INVENTION

It is an object of this invention to provide a process for producing an encapsulated crosslinking agent.

It is another object of this invention to provide an encapsulated crosslinking agent.

It is another object of this invention to provide a process for producing a gel-forming composition, said process comprising mixing an encapsulated crosslinking agent, a second polymer, and a ligand.

It is still another object of this invention to provide a gel-forming composition.

It is yet another object of this invention to provide a process for injecting a gel-forming composition into a subterranean formation.

In one embodiment of this invention, a process is provided for producing an encapsulated crosslinking agent comprising (or optionally, "consisting essentially of", or "consisting of") encapsulating a crosslinking agent with a first polymer.

In another embodiment of this invention, an encapsulated crosslinking agent is provided comprising (or optionally, "consisting essentially of" or "consisting of") a first polymer and a crosslinking agent, wherein said crosslinking agent is encapsulated by said first polymer.

In another embodiment of this invention, a process for producing a gel-forming composition is provided, said process comprising (or optionally, "consisting essentially of" or "consisting of") mixing an encapsulated crosslinking agent,

a second polymer, and a liquid, wherein said encapsulated crosslinking agent, said second polymer, and said liquid are each present in said gel-forming composition in an amount effective to form a gel.

5 In yet another embodiment of this invention, a gel-forming composition is provided comprising (or optionally, "consisting essentially of" or "consisting of") an encapsulated crosslinking agent, a second polymer, and a liquid wherein said encapsulated crosslinking agent, said second polymer, and liquid are each present in said gel-forming composition in an amount effective to form a gel.

10 Still another embodiment of this invention, a process is provided comprising (or optionally, "consisting essentially of" or "consisting of") injecting a gel-forming composition into a subterranean formation, wherein said gel-forming composition comprises an encapsulated crosslinking agent, a second polymer, and a liquid.

15 These objects and other objects of this invention will become more apparent with reference to the following.

**DETAILED DESCRIPTION OF THE
INVENTION**

In one embodiment of this invention, a process for producing an encapsulated crosslinking agent is provided, said 20 process comprising encapsulating a crosslinking agent with a first polymer.

25 Any crosslinking agent that is capable of crosslinking with a second polymer can be used in the process of the present invention. Said second polymer is discussed later in this disclosure. Generally, said crosslinking agent is selected from the group consisting of multivalent metallic compounds and organic crosslinking agents. The presently preferred multivalent metal compound is a metal compound selected from the group consisting of a complexed zirconium compound, a complexed titanium compound, a complexed chromium compound, a complexed aluminum compound, a complexed tin compound, a complexed iron compound, and mixtures thereof. The term "complexed" as used in this disclosure means a compound formed by the union of a metal ion with a nonmetallic ion or molecule 30 called a ligand. Suitable multivalent metallic compounds are selected from the group consisting of zirconium citrate, zirconium tetrachloride, zirconium oxychloride, zirconium complex of hydroxyethyl glycine, ammonium zirconium fluoride, zirconium 2-ethylhexanoate, zirconium acetate, zirconium tartarate, zirconium malonate, zirconium propionate, zirconium neodecanoate, zirconium acetylacetone, tetrakis(triethanolamine)zirconate, zirconium carbonate, ammonium zirconium carbonate, zirconyl ammonium carbonate, zirconium lactate, titanium acetylacetone, titanium ethylacetoacetate, titanium citrate, titanium triethanolamine, ammonium titanium lactate, aluminum citrate, chromium nitrate, chromium chloride, chromium citrate, chromium acetate, chromium propionate, and combinations of any two or more thereof. The presently most preferred crosslinking agent is selected from the group 35 consisting of chromium chloride, chromium propionate, chromium acetate, zirconium acetylacetone, zirconium tetrachloride, zirconium oxychloride, zirconium lactate, zirconium citrate, zirconium malonate, tetrakis(triethanolamine)zirconate, zirconium propionate, titanium acetylacetone, titanium ethylacetoacetate, titanium citrate, titanium triethanolamine, and combinations of any two or more thereof. These compounds are most preferred since they are readily available and form strong gels.

40 45 50 55 60 65 An organic crosslinking agent can also be utilized in said gel-forming composition. For example, said organic crosslinking agent can be selected from the group consisting

of formaldehyde; precursors of formaldehyde, such as, hexamethylenetetramine; furfuryl alcohol; aminobenzoic acid; phenol and phenolic derivatives, such as, hydroquinone, phloroglucinol, catechol, resorcinol, salicylic acid, salicylamide, and vanillin. A more detailed description of organic crosslinking agents can be found in U.S. Pat. Nos. 5,399,269 and 5,480,933, herein incorporated by reference.

Said first polymer can be any polymer that can degrade over a period of time to release said crosslinking agent. Said first polymer selected varies depending on the gelation rate desired. Degradation of said first polymer can occur, for example, by hydrolysis, solvolysis, melting, or other mechanisms. Preferred first polymers are selected from the group consisting of homopolymers and copolymers of glycolate and lactate, polycarbonates, polyanhidrides, polyorthoesters, and polyphosphacenes. Most preferably, said first polymer is poly(lactic acid-co-glycolic acid).

Said crosslinking agent is encapsulated by said first polymer by any method known in the art. For example, said encapsulation can be accomplished by a method selected from the group consisting of a double emulsion technique and a spray drying technique. Generally, said double emulsion technique involves the evaporation of a secondary emulsion by freeze drying or other drying method. For example, to prepare said encapsulated crosslinking agent, a first aqueous solution of said crosslinking agent to be encapsulated is emulsified in a first organic compound containing said first polymer to produce a primary emulsion. Said first organic compound can be any organic compound capable of placing a majority of said first polymer in solution. For example, said first organic compound can be selected from the group consisting of dichloromethane, ethyl acetate, cyclohexane, and mixtures thereof. Most preferably, said first organic compound is selected from the group consisting of dichloromethane and ethyl acetate, since these organic compounds have low boiling points and are not miscible in water. The primary emulsion can be produced by any mixing method known in the art. For example, said primary emulsion can be prepared by using mechanical mixing equipment.

The primary emulsion is then dispersed in a second aqueous solution, and then emulsified to produce said secondary emulsion. Said second aqueous solution includes hydrophilic stabilizers, such as, but not limited to, polyvinyl alcohol and surfactants. Polyvinyl alcohol is most preferred since it forms stable emulsions. The secondary emulsion is then evaporated by freeze drying or other method to remove said first organic compound and said second aqueous solution leaving said encapsulated crosslinking agent.

Spraying drying involves the atomization of a liquid feedstock comprising said first polymer and said crosslinking agent into a spray of droplets. The droplets are typically dried with hot air in a drying chamber. Generally, the spray is produced by rotary or nozzle atomizers.

In another embodiment of this invention, said encapsulated crosslinking agent is provided comprising said first polymer and said crosslinking agent, wherein said crosslinking agent is encapsulated with said first polymer. Said crosslinking agent and said first polymer were previously discussed in this disclosure.

In another embodiment of this invention, a process for producing a gel-forming composition is provided, said process comprising mixing an encapsulated crosslinking agent, a second polymer, and a liquid, wherein said second polymer, said encapsulated crosslinking agent, and said liquid are each present in said gel-forming composition in an amount effective to form a gel.

The gel-forming composition can also comprise a clay which can cause a water- or oil-based fluid to become

viscous. Examples of suitable clays include, but are not limited to, kaolinite, halloysite, vermiculite, chlorite, attapulgite, smectite, montmorillonite, illite, saonite, sepiolite, palygorskite, Fuller's earth, and combinations of any two or more thereof. The presently preferred clay is montmorillonite clay. The presently most preferred clay is sodium montmorillonite, which is also known as bentonite, since it is readily available and effective. Based on the total weight of the gel-forming composition, the clay can be present in the gel-forming composition in the range of about 0.25 weight % to about 30 weight %, preferably, in the range of about 0.5 weight % to about 25 weight %, and most preferably, in the range of 1 weight % to 20 weight %.

Any known weighting agent that can be suspended in said gel-forming composition can also be used in the present invention. A weighting agent is added to said gel-forming composition to increase the density. Weighting agents are utilized, for example, when said gel-forming composition is needed to block a gas release during drilling.

Examples of suitable weighting agents include, but are not limited to barite, hematite, calcium carbonate, galena, or combinations of any two or more thereof. The presently preferred weighting agent is barite for it is readily available and effective. The weighting agent can be present in the gel-forming composition in the range of about 5 to about 30 pounds of weighting agent per gallon of gel-forming composition, preferably, in the range of about 8 to about 25, and most preferably, in the range of 10 to 20.

Said encapsulated crosslinking agent was previously discussed in this disclosure. The concentration of encapsulated crosslinking agent used in the present invention depends largely on the desired gelation rate. It can also depend on the concentrations of said second polymer in the gel-forming composition, on the operation conditions, or the depth of the desired location in said subterranean formation. The concentration of crosslinking agent from degraded encapsulated crosslinking agent varies generally over the broad range of about 1 mg of said crosslinking agent per liter of gel-forming composition to about 20,000 mg of said crosslinking agent per liter of gel-forming composition, preferably, in the range of about 1 mg/l to about 10,000 mg/l, and most preferably, in the range of 1 mg/l to 5,000 mg/l.

Said second polymer can be any polymer that can form a gel when employed in the presence of said crosslinking agent and said liquid. The presently preferred second polymer is a carboxylate-containing polymer due to its availability and ease of use in this invention.

The term "carboxylate-containing polymer" used herein refers to a polymer that contains at least one free carboxylic group or a carboxylate group in which the proton of the carboxylic acid is substituted with an ammonium radical, an alkali metal, an alkaline earth metal, or combinations of two or more thereof.

According to the present invention, the weight average molecular weight of said carboxylate-containing polymers can be in the range of about 10,000 to about 30,000,000, preferably in the range of about 10,000 to about 25,000,000, and most preferably, in the range of 10,000 to 20,000,000. Said second polymers having weight average molecular weights greater than about 30,000,000 can cause said gel-forming compositions to be too dense causing problems with injecting said gel-forming compositions into subterranean formations.

Said second polymers having weight average molecular weights less than about 10,000 may not allow said gel-forming compositions to form strong gels. The mole percent (%) of the carboxylate group is generally in the range of from about 0.01 to about 30%, preferably, in the range of about 0.01 to about 20%, and most preferably, in the range of 0.1 to 10%. Said second polymers with greater than about 30 mole % carboxylate groups can cause said gel-

forming compositions to gel too fast while second polymers with less than about 0.01% carboxylate groups can cause said gel-forming compositions to form weak gels.

Carboxylate-containing polymers suitable for use in this invention are those capable of gelling in the presence of said crosslinking agent. For example, said carboxylate-containing polymers suitable for use in this invention are selected from the group consisting of cellulose ethers, biopolysaccharides, and acrylamide-containing polymers.

Suitable cellulose ethers are disclosed in U.S. Pat. No. 3,727,688, herein incorporated by reference. Particularly preferred cellulose ethers include carboxymethylhydroxyethyl cellulose (CMHEC) and carboxymethyl cellulose (CMC) for their ready availability.

Suitable biopolysaccharides are disclosed in U.S. Pat. No. 4,068,714, herein incorporated by reference. Particularly preferred is polysaccharide B-1459 and xanthan gums which are biopolysaccharides produced by the action of *Xanthomonas campestris* bacteria. This biopolysaccharide is commercially available in various grades under the tradename of, for example, "FLOWZAN" (Drilling Specialties Company, Bartlesville, Okla. which is readily available).

Suitable acrylamide-containing polymers which also contain carboxylate groups are disclosed in U.S. Pat. No. 3,749,172, herein incorporated by reference. Particularly preferred are the partially hydrolyzed polyacrylamides possessing carboxylate groups through which crosslinking can take place. Polyacrylamides generally can become hydrolyzed under a subterranean formation condition to produce at least one crosslinkable carboxylate group and thus can also be used in the present invention. Particularly preferred acrylamide-containing polymers for use in applications in high salinity environments at elevated temperatures are thermally stable carboxylate-containing polymers of acrylamide, partially hydrolyzed polyacrylamide, such as, copolymers of N-vinyl-2-pyrrolidone and acrylamide; copolymers of sodium-2-acrylamido-2-methylpropanesulfonate, acrylamide, and N-vinyl-2-pyrrolidone; copolymers of acrylamide, sodium-2-acrylamido-2-methylpropanesulfonate, and sodium acrylate; copolymers of sodium-2-acrylamido-2-methylpropanesulfonate and acrylamide; and copolymers of sodium-2-acrylamido-2-methylpropanesulfonate, acrylamide, N-vinyl-2-pyrrolidone, and sodium acrylate. Selected carboxylate-containing copolymers also are useful in the present process, such as copolymers derived from acrylamide, which are partially hydrolyzed to acrylate, and N-vinyl-2-pyrrolidone comonomers with lesser amounts of termonomers such as vinyl acetate, vinylpyridine, styrene, methyl methacrylate, and other polymers containing acrylate groups.

Other miscellaneous polymers suitable for use as said second polymer in the present invention include, but are not limited to, partially hydrolyzed polyacrylonitriles, copolymers of acrylate and styrene sulfonate, or combinations of any two or more thereof.

Though any second polymer that is crosslinkable and gellable can be used in the present invention, the presently preferred polymers are carboxylate-containing polymers selected from the group consisting of CMHEC, CMC, xanthan gum, acrylamide-containing polymers, or combinations of any two or more thereof.

The concentration or amount of said second polymer in the gel-forming composition can range widely depending on the gelation rate needed for a particular formation condition and the type of formation. Generally, the concentration of said second polymer in said gel-forming composition is in the range of about 100 mg of said second polymer per liter of said gel-forming composition to about 100,000 mg of said

second polymer per liter of said gel-forming composition, preferably, in the range of about 200 mg/l to about 70,000 mg/l, and most preferably, in the range of 200 mg/l to 50,000 mg/l. The preferred ranges produce acceptable gels at a reasonable cost.

Any suitable procedures for preparing an aqueous admixture of said second polymer can be used. Some of said second polymers can require particular mixing conditions, such as slow addition of finely powdered second polymer into a vortex of stirred brine, alcohol prewetting, protection from air (oxygen), and preparation of stock solutions from fresh rather than salt water.

Liquid generally makes up the rest of said gel-forming composition. Generally, water is used as said liquid since it is typically most economical in oil field applications. Water includes, but is not limited to, pure water, regular tap water, sea water, a solution or suspension wherein the solution or suspension contains a variety of salts, and a produced brine. Produced brine is defined as the brine co-produced with oil or gas, or both. Generally, produced brine is a hard brine, i.e., containing at least 1,000 ppm by weight of Ca²⁺, Ba²⁺, Mg²⁺, or Sr²⁺, or combinations of two or more thereof. A produced brine generally contains high salinity of from about 1% by weight to about 30% by weight total dissolved solids. A produced brine generally is contaminated with oil or gas, or both. Said second polymer generally gels well in produced brines having a salinity of from about 0.3% by weight to about 27% by weight.

The gel-forming composition of the present invention, before it is injected into a subterranean formation, can be an aqueous solution, a suspension comprising undissolved solids, gas, or oil, or combinations of two or more thereof. Upon mixing the components of the gel-forming composition, the composition can be substantially gelless, microgels, bulk gels, or combinations of any two or more thereof, which can be flowing or can travel to a desired location in a subterranean formation. However, once the gel-forming composition completes gelation, the composition becomes a nonflowable gel.

In another embodiment of this invention, a gel-forming composition is provided comprising said encapsulated crosslinking agent, said second polymer and a liquid, wherein said second polymer, said encapsulated crosslinking agent, and said liquid are each present in said gel-forming composition in an amount effective to form a gel. Said encapsulated crosslinking agent, second polymer, and said liquid have been previously described in this disclosure.

According to yet another embodiment of the present invention, a process is provided comprising injecting said gel-forming composition into a subterranean formation. Said gel-forming composition can be injected sequentially or simultaneously. In sequential injection, said encapsulated crosslinking agent in said liquid and said second polymer in said liquid are injected separately. Alternatively, in simultaneous injection, said encapsulated crosslinking agent, said second polymer, and said liquid can be mixed prior to injection.

The amount of said gel-forming composition injected can vary widely depending on the treatment required or desired. Generally, the process, i.e., the injection of said gel-forming composition, can be utilized for numerous functions. Said gel-forming composition is used in oil field operations to alter the permeability of said subterranean formation. For example, said gel-forming composition can be utilized to enhance the efficiency of water flooding or carbon dioxide injection in enhanced oil recovery processes, to plug fractures or channels, to prevent loss of drilling fluids, and to block gas release during drilling.

The nature of the subterranean formation is not critical to the practice of the process of the present invention. Said

gel-forming composition can be injected into said subterranean formation having a temperature range of from about 10° C. to about 180° C. Most preferably, said subterranean formation has a temperature in the range of 10° C. to 150° C. Any means known to one skilled in the art such as, for example, pumps, can be used for injecting said gel-forming composition.

EXAMPLES

These examples are provided to further illustrate the invention.

Example 1

5 milliliters of distilled water was added to a solution of 1 gram of poly(lactic acid-co-glycolic acid) obtained as Resomer® RG506 (from Boehringer Ingelheim in Germany) and 0.836 grams of 99 wt % zirconium acetylacetone (obtained from Strem Chemicals, Inc., MA, USA) in 20 milliliters of dichloromethane. The solution was emulsified by using an Ultra-Turrax T25 mixer (obtained from Janke & Kunkel IKA Labortechnik in Germany) at 8000 revolutions per minute (rpm) for 60 seconds to produce a primary emulsion. The primary emulsion was then dispersed into a 200 milliliter aqueous solution of 0.2 wt % polyvinyl alcohol in distilled water and emulsified by using the Ultra-Turrax mixer at 8000 rpm for 30 seconds to produce a secondary emulsion. An ice-bath was used to cool said solution, primary emulsion, and secondary emulsion during the emulsification process. The polyvinyl alcohol was evaporated for 3 hours at room temperature under vigorous stirring. Encapsulated zirconium acetylacetone particles were collected by centrifugation, washed twice with distilled water, and left overnight before they were freeze-dried. The zirconium content of the encapsulated zirconium acetylacetone particles was 0.8 grams or 5 wt % as measured using X-ray fluorescence. A Siemens SRS 303AS wavelength dispersive spectrometer was used to make the zirconium content analyses.

Poly(acrylamide-co-acrylic acid) was dissolved in synthetic North Sea water (SNSW) to form a second solution. The poly(acrylamide-co-acrylic acid) was obtained as Alcoflood 935 from Allied Colloids Ltd, England having 10% acrylic acid and a molecular weight of 9,000,000. The SNSW had the following composition: NaHCO₃—0.205 g/l; Na₂SO₄—4.288 g/l; NaCl—23.834 g/l; CaCl₂·2H₂O—1.645 g/l; MgCl₂·6H₂O—10.774 g/l in distilled water.

Encapsulated zirconium acetylacetone particles, produced as described earlier in this example, were added to said second solution to produce a gel-forming composition and placed in glass ampoules. The head space of the glass ampoules was evacuated with an inert gas and sealed with a torch. The gel-forming composition was shaken at ambient temperature for 30 minutes and then heated at 50° C. for 13 days and subsequently at 80° C. for 35 days while observed regularly by visual inspection.

The data are shown in Table 1. At 50° C. for 13 days, no gel formed. However, after 12 days at 80° C., a strong gel formed. These data show that an encapsulated crosslinking agent slows the gelation rate of gel-forming compositions.

Comparative Example 1

Gel-forming compositions consisting of varying concentrations of unencapsulated zirconium acetylacetone and poly(acrylamide-co-acrylic acid) obtained as Alcoflood 935 from Allied Colloids Ltd, England in SNSW were made and placed in glass ampoules. The head space of the glass ampoules was evacuated using an inert gas and then sealed by a torch. Said gel-forming compositions formed gels within less than one day at ambient temperatures.

The data are shown in Table 2. Example 1 and Comparative Example 1 illustrate that encapsulation of said crosslinking agent extends the gelation rate of gel-forming compositions. In Example 1, gels were not formed when said gel-forming compositions were heated to 50° C. for 13 days. However, in Comparative Example 1, gels formed at ambient temperatures in less than one day from gel-forming compositions with unencapsulated crosslinking agent.

Example 2

The same procedure as utilized in Example 1 was followed except 0.418 grams of zirconium acetylacetone were added, and the ampoules were heated at 50° C. for 2 days and subsequently at 80° C. for 50 days. The zirconium content of the encapsulated zirconium acetylacetone particles was 0.6 grams or 3 wt % as measured using X-ray fluorescence. The data are shown in Table 3.

A gel-forming composition containing 209 ppm by weight total zirconium and 0.75 wt % poly(acrylamide-co-acrylic acid) formed a gel after 10 days at 80° C. Thus, showing the delayed gelation rate caused by said encapsulated crosslinking agents.

TABLE 1

Gel-test with Alcoflood 935 and encapsulated zirconium acetylacetone in SNSW at 50–80° C.

		Gelling Conditions						Gelling Results					
		Second			50° C.			80° C.					
Total Amount of Zirconium (ppm by wt.)	Polymer conc. (wt %)	13 days	4 days	5 days	6 days	12 days	35 days	NG	VWG ¹	WG ¹	STG ¹	VWG ¹	RG ¹
269	0.7	NG	NG	VWG ¹	WG ¹	STG ¹	VWG ¹	NG	NG	VWG ¹	STG ¹	VWG ¹	RG ¹
393	0.7	NG	NG	VWG ¹	WG ¹	STG ¹	STG ¹	NG	NG	VWG ¹	STG ¹	VWG ¹	RG ¹

NG = No gel,
VWG = Very weak gel,
WG = Weak gel,
STG = strong gel,
RG=Rigid gel.
¹Gel without liquid.

TABLE 2

Gel-test with Alcoflood 935 and unencapsulated zirconium acetylacetone in SNSW			
Gelling Conditions			
Conc. of Zr (ppm by wt.)	Second Polymer	Conc. (wt %)	Gelling Results
595	0.5		weak gel
228	1.0		slight gel
280	1.0		slight gel
465	1.0		strong gel
465	1.0		strong gel
701	1.0		strong gel
744	1.0		rigid gel

TABLE 3

Gel-test with Alcoflood 935 and encapsulated zirconium acetylacetone in SNSW at 50-80°C.								
Gelling Conditions								
Total Amount	Second Polymer	50°C.	Gelling Results					
of Zirconium (ppm by wt.)	Polymer conc. (wt %)	50°C.	2 days	2 days	4 days	10 days	23 days	50 days
110	0.5	NG	NG	NG	NG	NG	NG	NG
206	0.5	NG	NG	NG	WG ^b	WG ^b	WG ^b	WG ^b
231	0.5	NG	NG	NG	WG ^b	WG ^b	WG ^b	NG
209	0.75	NG	NG	NG	RG ^c	RG ^c	RG ^c	VWG ^d
313	0.75	NG	NG	NG	WG ^b	RG ^c	RG ^c	RG ^c
415	0.75	NG	NG	NG	VWG ^d	RG ^c	RG ^c	RG ^c

NG = No gel,

VWG = Very weak gel,

WG = Weak gel,

RG = Rigid gel.

^aGel without liquid.^bGel with 15% liquid expelled.^cGel with 40% liquid expelled.

That which is claimed is:

1. A process for producing an encapsulated crosslinking agent comprising the steps of:

(a) emulsifying a first aqueous solution containing the crosslinking agent with a first organic compound containing a first polymer thereby producing a primary emulsion;

(b) dispersing the primary emulsion into a second aqueous solution;

(c) emulsifying said solution of step (b) thereby producing a secondary emulsion; and

(d) drying said secondary emulsion thereby producing an encapsulated crosslinking agent;

wherein said crosslinking agent is selected from the group consisting of multivalent metallic compounds and organic crosslinking agents and said first polymer is poly(lactic acid-co-glycolic acid).

2. A process according to claim 1 wherein said crosslinking agent in zirconium acetylacetone.

3. A process for producing an encapsulated crosslinking agent comprising the steps of:

45 4. A process to claim 3 wherein said crosslinking agent is zirconium acetylacetone.

5. A process for producing a gel-forming composition, said process comprising mixing a zirconium compound crosslinking agent encapsulated in poly(lactic acid-co-glycolic acid), a second polymer, and a liquid.

6. A process for producing a gel-forming composition according to claim 5 wherein the concentration of said crosslinking agent from degraded encapsulated crosslinking agent ranges from about 1 mg of crosslinking agent per liter of gel-forming composition to about 20,000 mg of crosslinking agent per liter of gel-forming composition.

7. A process for producing a gel-forming composition according to claim 6 wherein said second polymer is a carboxylate-containing polymer.

8. A process for producing a gel-forming composition according to claim 7 wherein the concentration of said second polymer ranges from about 100 mg of said second polymer per liter of said gel-forming composition to about 100,000 mg of said second polymer per liter of said gel-forming composition.

65 9. A process for producing a gel-forming composition according to claim 8 wherein the concentration of said crosslinking agent from degraded encapsulated crosslinking

agent ranges from about 1 mg of said crosslinking agent per liter of said gel-forming composition to about 10,000 mg of said crosslinking agent per liter of said gel-forming composition.

10. A process for producing a gel-forming composition according to claim 9 wherein said carboxylate-containing polymer are selected from the group consisting of cellulose ethers, biopolysaccharides, and acrylamide-containing polymers.

11. A process for producing a gel-forming composition according to claim 10 wherein the concentration of said second polymer ranges from about 200 mg of said second polymer per liter of said gel-forming composition to about 70,000 mg of said second polymer per liter of said gel-forming composition.

12. A process for producing a gel-forming composition according to claim 11 wherein the concentration of said crosslinking agent ranges from 1 mg of said crosslinking agent from degraded encapsulated crosslinking agent per liter of said gel-forming composition to 5,000 mg of said crosslinking agent per liter of said gel-forming composition.

13. A process for producing a gel-forming composition according to claim 12 wherein said carboxylate-containing polymers are selected from the group consisting of carboxymethylhydroxyethyl cellulose, carboxymethyl cellulose, xanthan gum, acrylamide-containing polymers, and combinations of any two or more thereof.

14. A process for producing a gel-forming composition according to claim 13 wherein the concentration of said second polymer ranges from 200 mg of said second polymer per liter of said gel-forming composition to 50,000 mg of said second polymer per liter of said gel-forming composition and wherein said second polymer is poly(acrylamide-co-acrylic acid).

15. A gel-forming composition comprising a zirconium compound crosslinking agent encapsulated in poly(lactic acid-co-glycolic acid), a second polymer, and a liquid wherein said second polymer, said encapsulated crosslinking agent, and said liquid are each present in said gel-forming composition in an amount effective to form a gel.

16. A gel-forming composition according to claim 15 further comprising a clay which can cause a water- or oil-based fluid to become viscous.

17. A gel-forming composition according to claim 15 further comprising a weighting agent.

18. A process comprising injecting a gel-forming composition into a subterranean formation, wherein said gel-forming composition comprises a zirconium compound crosslinking agent encapsulated in poly(lactic acid-co-glycolic acid), a gellable second polymer and a liquid.

19. A process according to claim 1 wherein said drying of step (d) comprises spray drying.

20. A process according to claim 3 wherein said crosslinking agent is selected from the group consisting of chromium chloride, chromium propionate, chromium acetate, zirconium acetylacetone, zirconium tetrachloride, zirconium oxychloride, zirconium lactate, zirconium citrate, zirconium malonate, tetrakis(triethanolamine)zirconate, zirconium complex of hydroxyethyl glycine, zirconium tartarate, zirconium propionate, titanium acetylacetone, titanium ethylacetate, titanium citrate, titanium triethanolamine, and combinations of any two or more thereof.

21. A process according to claim 20 wherein said first polymer is copolymer of glycolate and lactate.

22. A process according to claim 21 wherein said drying of step (d) comprises spray drying.

* * * * *

**APPENDIX F: CITED OPINIONS OF THE BOARD OF PATENT
APPEALS AND INTERFERENCES**

Contents:

1. *Ex parte Levy*, 17 USPQ2d 1461, 1464 (Bd. Pat. App. & Inter. 1990)

**C**

Ex parte Levy

U.S. Patent and Trademark Office Board of Patent
Appeals and Interferences
No. 90-1864

Decided October 16, 1990

Released November 8, 1990

United States Patents Quarterly Headnotes

PATENTS

[1] Patentability/Validity - Anticipation - Identity of elements (§ 115.0704)

Factual determination of anticipation requires disclosure in single reference of every element of claimed invention, and examiner must identify wherein each and every facet of claimed invention is disclosed in applied reference.

PATENTS

[2] Patentability/Validity - In general (§ 115.01)

Patentability/Validity - Anticipation - Prior art (§ 115.0703)

Initial burden of establishing prima facie basis to deny patentability rests upon examiner; examiner, if relying upon theory of inherency, must provide basis in fact and/or technical reasoning to reasonably support determination that allegedly inherent characteristic necessarily flows from teachings of applied prior art.

PATENTS

[3] Patentability/Validity - Anticipation - Prior art (§ 115.0703)

Examiner erred by rejecting claims for biaxially oriented catheter balloon as anticipated by prior art which does not disclose such biaxially oriented balloon and which has not been shown to be inherently biaxially oriented.

PATENTS

[4] Patentability/Validity - Obviousness - Relevant prior art - Particular inventions (§ 115.0903.03)

Examiner erred by rejecting claims for biaxially

oriented balloon catheter under 35 USC 103 based upon combined disclosure of two prior art references, one of which was relied upon solely for disclosed use of high viscosity polyethylene terephthalate tubing and the other which was presupposed by examiner to disclose biaxially oriented catheter balloon, since examiner has not established that resulting catheter balloon using high viscosity tubing is biaxially oriented.

Application of Stanley B. Levy, serial no. 287,234, filed Dec. 21, 1988, which is a division of serial no. 914,108, filed Oct. 1, 1986, now Re. 32,983, granted July 4, 1989; and a reissue of serial no. 510,812, filed July 5, 1983, now patent no. 4,490,421, granted Dec. 25, 1984, for balloon and manufacture thereof. From examiner's rejection of claims 13 through 17 and 25 (James Seidleck, primary examiner), applicant appeals. Reversed.

Louis H. Rombach, Wilmington, Del., for appellant.

Before Steiner, Tarring, and J. Smith, examiners-in-chief.

Steiner, examiner-in-chief.

This is an appeal from the final rejection of claims 13 through 17 and 25, which are all of the claims remaining in this application for reissue of U.S. Patent No. 4,490,421.

The subject matter on appeal is directed to a polymeric balloon exhibiting properties which enable its use as a catheter balloon for medical dilation procedures, such as coronary angioplasty wherein a catheter with a balloon at a distal end thereof is inserted into coronary arteries and inflated. The balloon must be capable of exerting sufficient pressure to dilate stenotic lesions without rupture of the balloon.

Claims 13 and 25, the only independent claims on appeal, read as follows:

13. *High molecular weight, biaxially oriented, flexible polymeric balloon having a wall tensile strength of at least 31,714 psi (218.86 MPa).*

25. *High molecular weight, biaxially oriented, flexible*

polyethylene terephthalate dilatation catheter balloon.

Wyeth et al. (Wyeth)	3,733,309	May 15, 1973
Schjeldahl et al.		
(Schjeldahl '989)	4,413,989	Nov. 8, 1983 ¹
Schjeldahl et al.		
(Schjeldahl '000)	4,456,000	June 26, 1984 ²

Claims 13, 14, 16, 17 and 25 stand rejected under 35 U.S.C. 102 as anticipated by Schjeldahl. Claims 13 through 17 stand rejected under 35 U.S.C. 103 based upon "Schjeldahl et al in view of Wyeth as set forth in the Final Rejection" (paragraph bridging pages 3 and 4 of the Answer). We reverse each rejection.

The Rejection of Claims 13, 14, 16, 17 and 25 Under 35 U.S.C. §102.

[1] The factual determination of anticipation requires the disclosure in a single reference of every element of the claimed invention. *In re Spada*, - F.2d -, 15 USPO2d 1655 (Fed. Cir. 1990); *In re Bond*, - F.2d -, 15 USPO2d 1566 (Fed. Cir. 1990); *Diversitech Corp. v. Century Steps, Inc.*, 850 F.2d 675, 7 USPO2d 1315 (Fed. Cir. 1988); *Constant v. Advanced Micro-Devices, Inc.*, 842 F.2d 1560, 7 USPO2d 1057 (Fed. Cir. 1988); *Alco Standard Corp. v. TVA*, 808 F.2d 1490, 1 USPO2d 1337 (Fed. Cir. 1986); *In re Marshall*, 578 F.2d 301, 198 USPO 344 (CCPA 1978); *In re Arkley*, 455 F.2d 586, 172 USPO 524 (CCPA 1972). Moreover, it is incumbent upon the examiner to identify wherein each and every facet of the claimed invention is disclosed in the applied reference. *Lindemann Maschinenfabrik GmbH v. American Hoist and Derrick*, 730 F.2d 1452, 221 USPO 481 (Fed. Cir. 1984).

Each of the independent claims on appeal defines a polymeric balloon which is "biaxially oriented." Ergo, in order to establish a *prima facie* basis to defeat the patentability of independent claims 13 and 25 under 35 U.S.C. § 102, the examiner is obliged to point out where Schjeldahl discloses a *biaxially oriented* polymeric balloon. The tenor of the final rejection and Answer presupposes that Schjeldahl discloses a biaxially oriented polymeric balloon. See, for example, page 5 of the Final Rejection wherein

The references relied upon by the examiner are:

May 15, 1973

Nov. 8, 1983 ¹

June 26, 1984 ²

the examiner states

[t]he reference clearly teaches a biaxially oriented balloon catheter, and states that it is made by injection blow molding.

See, also, page 5 of the Answer wherein the examiner states

[a]rguments that the references don't disclose a biaxially oriented PET (polyethylene terephthalate) balloon catheter is contrary to what is *clearly stated* in the references (emphasis supplied).

The examiner does not point to, and we do not find, any express disclosure in Schjeldahl of a biaxially oriented polymeric balloon.

It would appear that the relevant evulgations in Schjeldahl which may have led the examiner to his determination are:

(a) an expander ^{EN3} formed from a thin, flexible inelastic, high tensile strength, *biaxially oriented* synthetic plastic material *1463 (column 2 of Schjeldahl '989, lines 63 through 65, emphasis supplied);

(b) The expander 30 is preferably formed from a suitable synthetic plastic material, such as *biaxially oriented* polypropylene, by an *injection blow molding operation* and, as such, is substantially inelastic in both the axial and radial directions and may, for example, have a finished wall thickness in the range of from 0.005 to 0.200 millimeters, 0.025 millimeters being typical (column 6 of Schjeldahl '989, lines 45 through 52, emphasis supplied);

(c) It has been found that an expander of the above-dimensional characteristics can withstand internal inflation pressure in excess of 7 atmospheres without fear of rupture (column 6 of Schjeldahl '989, lines 62 through 65);

(d) injection blow molding step used to form the expander 30 (column 8, lines 16 and 17);

(e) the expander 30 is formed from a biaxially oriented thin plastic material capable of withstanding relatively high internal pressures without rupture and without exceeding the elastic limit for the material itself (column 10 of Schjeldahl '989, lines 32 through 36, emphasis supplied);

(f) the expander 82 is preferably formed from a suitable synthetic plastic material such as biaxially oriented polypropylene or biaxially oriented polyethylene terephthalate by an injection molding operation and, as such, is substantially inelastic in both the axial and radial direction (column 12 of Schjeldahl '989, lines 22 through 37, emphasis supplied); and

(g) Apparatus as in claim 1 wherein said non-elastic expander member comprises a longitudinally extending thin, flexible, tubular element formed from a biaxially oriented synthetic plastic material surrounding said outer tubular member with opposed ends thereof secured to said outer tubular member at spaced apart locations proximate said distal end thereof (claim 8 of Schjeldahl '989, emphasis supplied).

These excerpts do not justify the determination that Schjeldahl discloses a biaxially oriented polymeric balloon.

According to Schjeldahl, the starting material is a biaxially oriented synthetic plastic material, such as polyethylene terephthalate. The final article, i.e., the expander or catheter balloon, is not characterized as biaxially oriented. Moreover, it would appear to be undisputed that the only method disclosed by Schjeldahl for transforming the biaxially oriented starting plastic into the final catheter balloon, i.e., injection blow molding, is not capable of producing a biaxially oriented catheter balloon. In fact, it is undisputed that injection blow molding would destroy the biaxial orientation of the plastic starting material. We refer to the Belcher affidavits, Exhibits V, VI and VIII, ^{EPA} which factually set forth the differences between "injection blow molding" and "injection stretch blow molding," and support the conclusion that the "injection blow molding" process disclosed by Schjeldahl could not possibly produce a biaxially oriented polymeric balloon. ^{EPA}

Indeed, the examiner agrees with appellant's position that injection blow molding could not produce a biaxially oriented balloon. See, for example, page 5

of the Final Rejection wherein the examiner states: [s]tatements that injection blow molding without stretching will not produce a biaxially oriented article are true... (emphasis supplied).

The examiner goes on, in the same sentence, to state: but since the reference produces a biaxially oriented article, clearly a stretching step must be used.

Again, on page 5 of the Answer, the examiner states: Since Schjeldahl et al produces a biaxially oriented article it follows that a stretching step must be used in the injection blow molding process.

The inescapable facts are that Schjeldahl does not disclose a biaxially oriented catheter balloon and does not mention a stretching step.

[2] The examiner also relies upon the theory that Schjeldahl's catheter balloon is inherently biaxially oriented. On page 4 of the Answer, the examiner points out that inasmuch as the Patent and Trademark Office does not have the requisite laboratory equipment for testing, the burden shifts to appellant. However, the initial burden of establishing a *prima facie* basis to deny patentability to a claimed invention rests *1464 upon the examiner. *In re Piascicki*, 745 F.2d 1468, 223 USPQ 785 (Fed. Cir. 1984). In relying upon the theory of inherency, the examiner must provide a basis in fact and/or technical reasoning to reasonably support the determination that the allegedly inherent characteristic necessarily flows from the teachings of the applied prior art. *In re King*, 801 F.2d 1324, 231 USPQ 136 (Fed. Cir. 1986); *W.L. Gore & Associates, Inc. v. Garlock, Inc.*, 721 F.2d 1540, 220 USPQ 303 (Fed. Cir. 1983); *In re Oelrich*, 666 F.2d 578, 212 USPQ 323 (CCPA 1981); *In re Wilding*, 535 F.2d 631, 190 USPQ 59 (CCPA 1976); *Hansgirg v. Kemmer*, 102 F.2d 212, 40 USPQ 665 (CCPA 1939). In our opinion, the examiner has not discharged that initial burden.

Schjeldahl does not provide any working example revealing the process conditions employed to produce the catheter balloon. We have only a general invitation to employ "injection blow molding." As previously discussed, it is undisputed that injection blow molding would not have produced a biaxially oriented balloon and would have destroyed the biaxial orientation of a polymeric starting material.

Schjeldahl does not disclose any particular tensile strength of the catheter balloon. We do not find sufficient factual basis or cogent scientific reasoning to support the conclusion that Schjeldahl's disclosure with respect to the ability of the catheter balloon to "withstand an internal inflation pressure in excess of 7 atmospheres without fear of rupture" (column 6 of Schjeldahl '989, lines 63 through 65) *necessarily* means that the catheter balloon is biaxially oriented. According to the membrane equation calculations reported in Levy's declaration (Exhibit IV), Schjeldahl's balloon could not possibly exhibit the tensile characteristics of a biaxially oriented balloon. Levy's calculations are *inconsistent* with those of Pinchuk (Exhibit III). Suffice it to say, the conflicting calculations taint the factual determination of inherency with impermissible conjecture. Indeed, the examiner, in the paragraph bridging pages 4 and 5 of the Answer, states that the membrane equation used to determine the tensile [sic, tensile] strength can be manipulated to produce any desired value, and thus is misleading.

Nevertheless, the examiner goes on to favor Pinchuk's calculations by stating in that same paragraph that [c]ertainly use of the typically used wall thickness disclosed in Schjeldahl et al with the average radius, as done in the Pinchuk Declaration would be reasonable.

As noted above, the conflicting results obtained by applying the membrane equation, and the examiner's acknowledgment that that equation "can be manipulated to produce any desired value," underscore the speculative nature upon which the determination of inherency rests.

We do not find sufficient cogent technical reasoning and/or objective evidence to support the conclusion that Schjeldahl's characterization of the catheter balloon as inelastic in the axial and radial direction *necessarily* means that the catheter balloon is biaxially oriented. The characteristic "inelastic," as employed by Schjeldahl, apparently means that the catheter balloon will expand to a preformed diameter to enable precise measurement of the pressures exerted on the inner wall of the artery during the dilation procedure (column 4 of Schjeldahl '989, lines 12 through 17).

[3] In summary, Schjeldahl does not disclose a biaxially oriented catheter balloon. We do not find a sufficient basis to support the determination that Schjeldahl's balloon is *inherently* (necessarily) biaxially oriented. *In re King, supra; W.L. Gore & Associates, Inc. v. Garlock, Inc., supra; In re Ulrich, supra; In re Wilding, supra; Hansgirg v. Kemmer, supra.* Accordingly, the examiner's rejection of claims 13, 14, 16, 17 and 25, under 35 U.S.C. § 102 as anticipated by Schjeldahl is reversed. ^{¶¶¶}

The Rejection of Claims 13 through 17 under 35 U.S.C. §103 Based upon the Combined Disclosures of Schjeldahl and Wyeth.

Wyeth is directed to producing high strength biaxially oriented polyethylene terephthalate beverage containers. The disclosed method involves stretching polyethylene terephthalate having a relatively high inherent viscosity, e.g., at least about 0.85.

*1465 It is apparent from the Final Rejection and Answer that the examiner's rejection of the appealed claims under 35 U.S.C. 103 is *not* predicated upon the theory that one having ordinary skill in the art would have been led to employ Wyeth's technique to produce a biaxially oriented balloon for use in Schjeldahl's catheter. Instead, the examiner presupposes that Schjeldahl discloses a biaxially oriented catheter balloon. The examiner relies upon Wyeth *solely* for the disclosed use of high viscosity polyethylene terephthalate tubing. We refer to page 6 of the Answer, first complete paragraph, wherein the examiner explains the rejection by stating: Wyeth et al is not being combined with Schjeldahl et al, but merely shows the claimed high viscosity PET (polyethylene terephthalate) and supports the examiners [sic, examiner's] inherency arguments. ^{¶¶¶}... The examiner is not substituting the process of Wyeth et al into Schjeldahl et al since both disclose the same process. ^{¶¶¶} Arguments that Wyeth et al can't be scaled down are irrelevant since the examiner is not seeking to scale down that reference to produce the claimed article.

[4] We have already concluded that the examiner factually erred in determining that Schjeldahl expressly or inherently discloses a biaxially oriented catheter balloon. Assuming, *arguendo*, the examiner

correctly concluded that one having ordinary skill in the art would have been led to employ a high viscosity polyethylene terephthalate tubing in producing Schjeldahl's catheter balloon, the rejection under 35 U.S.C. §103 must fall because the examiner has not established that the resulting catheter balloon is biaxially oriented. *Uniroyal, Inc. v. Rudkin-Wiley Corp.*, 837 F.2d 1044, 5 USPO2d 1434 (Fed. Cir., 1988).

Inasmuch as the examiner's rejection under 35 U.S.C. §103 is not predicated upon the theory that one having ordinary skill in the art would have been led to employ a conventional stretch blow molding technique, such as that disclosed by Wyeth, to produce Schjeldahl's catheter balloon, the motivation for such a combination is an issue which was not crystallized on appeal and was not confronted by appellant. However, in view of the examiner's gratuitous statement in the paragraph bridging pages 5 and 6 of the Answer, ^{fn8} we are constrained to address that issue.

There appears to be no dispute that one having ordinary skill in the art would have recognized the desirability of producing a biaxially oriented balloon for use in Schjeldahl's catheter, since biaxially oriented materials were known to exhibit high tensile strengths. The thrust of the evidence relied upon by the examiner is that one having ordinary skill in the art would have simply resorted to a conventional stretch molding technique to produce a biaxially oriented balloon for use in Schjeldahl's catheter, specifically, *the technique employed by Wyeth to produce a beverage container*. See paragraph 4 of the Rydell affidavit executed April 25, 1988 and offered in support of the protest in parent application Serial No. 914,108, paragraph 5 of the Pinchuk affidavit (Exhibit III), and paragraphs 4 and 5 of the Kaufman affidavit (Exhibit XII). Interestingly enough, *Wyeth disagrees*. See page 5 of Wyeth's declaration (Exhibit XI). Wyeth points out various differences between the PET bottles produced by his disclosed process and the requirements of a catheter balloon, and then concludes that his process could *not* be used to produce a catheter balloon of the type disclosed by Levy.

We are persuaded by Belcher's affidavits and Wyeth's declaration, notwithstanding the affidavits of Rydell, Pinchuk and Kaufman, ^{fn10} that the known processes

for producing^{*1466} biaxially oriented beverage containers, such as that disclosed by Wyeth, could not have been simply scaled down to produce a biaxially oriented catheter balloon for use in medical dilation procedures without the exercise of inventive skill.^{fn11} Based upon the record before us, it would appear unrealistic to conclude that one having ordinary skill in the art would have been led to employ Wyeth's technique, which is designed to produce beverage containers, to produce Schjeldahl's catheter balloon, motivated by a reasonable expectation of obtaining a biaxially oriented polymeric catheter balloon. *In re O'Farrell*, 853 F.2d 894, 7 USPO2d 1673 (Fed. Cir. 1988). The rejection under 35 U.S.C. §103 is also reversed.

REVERSED.

^{FN1} Each of the Schjeldahl references contains essentially the same relevant disclosure. Accordingly, unless otherwise indicated, we have referred to these references collectively as "Schjeldahl," consistent with the approach adopted by both appellant and the examiner.

^{FN2} See footnote 1.

^{FN3} Schjeldahl characterizes the catheter balloon as an expander.

^{FN4} Unless otherwise indicated, all exhibits mentioned are the exhibits to appellant's Brief.

^{FN5} We recognize that a high burden of proof is required to demonstrate the inoperability of a United States patent. *In re Weber*, 405 F.2d 1403, 160 USPO 549 (CCPA 1969); *In re Michalek*, 162 F.2d 229, 74 USPO 107 (CCPA 1947). However, as noted above, Schjeldahl does not disclose a catheter balloon made of a biaxially oriented plastic. Therefore, appellant's evidence is not an attack on the operability of Schjeldahl, but quite relevant to the issue of inherency, i.e., whether the catheter balloon disclosed by Schjeldahl is inherently biaxially oriented.

FN6 There is evidence of record that Dupont, the assignee of the application, furnished biaxially oriented polyethylene terephthalate to Schjeldahl when he informed Dupont personnel that he required a thin, high strength polymeric film having a tensile strength in the range of 20,000-40,000 psi. See the Schjeldahl affidavit (Exhibit VIII) and the Denglér declaration executed on May 21, 1988 and appended to the protest submitted in parent application Serial No. 914,108. Such facts are not inconsistent with our determination that Schjeldahl does not disclose a biaxially oriented polyethylene terephthalate catheter balloon. The Rydell affidavit appended to the protest in the parent application does not persuade us that Schjeldahl expressly or inherently discloses a biaxially oriented polymeric catheter balloon. See Belcher's affidavit (Exhibit VI).

FN7 Actually, according to the Final Rejection which is incorporated in the Answer,

[i]t is the Examiner's position that it would be *prima facie* obvious to use the high viscosity polyethylene terephthalate of Wyeth in Schjeldahl et al to produce the claimed product (page 4, the only complete paragraph).

FN8 It is apparent from our reversal of the examiner's rejection under 35 U.S.C. §102 that, in our opinion, Schjeldahl discloses neither a biaxially oriented catheter balloon nor a molding process which involves stretching.

FN9 The noted statement provides:

Certainly in the least there was an *invitation* to make a biaxially oriented catheter balloon at the time of the Schjeldahl et al invention. Additionally injection stretch blow molding to produce biaxially oriented articles was well known at the time of the Schjeldahl et al invention (emphasis supplied).

FN10 We agree with appellant that the credentials of Belcher and Wyeth in the relevant art appear more impressive than those of protestor's experts. According to the affidavit appearing as Appendix V, Belcher

authored the chapter called "Blow Molding of Polymers" for the fifth edition of the Plastic Engineering Handbook of the Society of Plastics Industry. In addition, Belcher authored two chapters, one on "injection blow molding" and one on "stretch blow molding" for the Blow Molding Handbook of the Society of Plastics and Engineers. We consider Wyeth's opinion with respect to the capabilities of his own invention entitled to greater weight than the opinions of Rydell, Pinchuk and Kaufman.

FN11 We find it somewhat unrealistic in light of the apparent disparities in size and function, Belcher's affidavits and Wyeth's declaration, that Pinchuk and Kaufman equate beverage bottles to catheter balloons. See paragraph 10 of the Pinchuk affidavit (Exhibit III), wherein it is stated

[a]s a blow molded polymeric article, a bottle and a catheter balloon are equivalent.
See, also, paragraph 4 of the Kaufman affidavit (Exhibit XII), wherein it is stated that anyone with ordinary skill in the plastics art would know how to make a biaxially oriented PET balloon; it would be similar to making a biaxially oriented PET bottle because both catheter balloons and bottles are equivalent structures - they are both fluid containers.

P.T.O. Bd.Pat.App. & Int.

Ex Parte Levy

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